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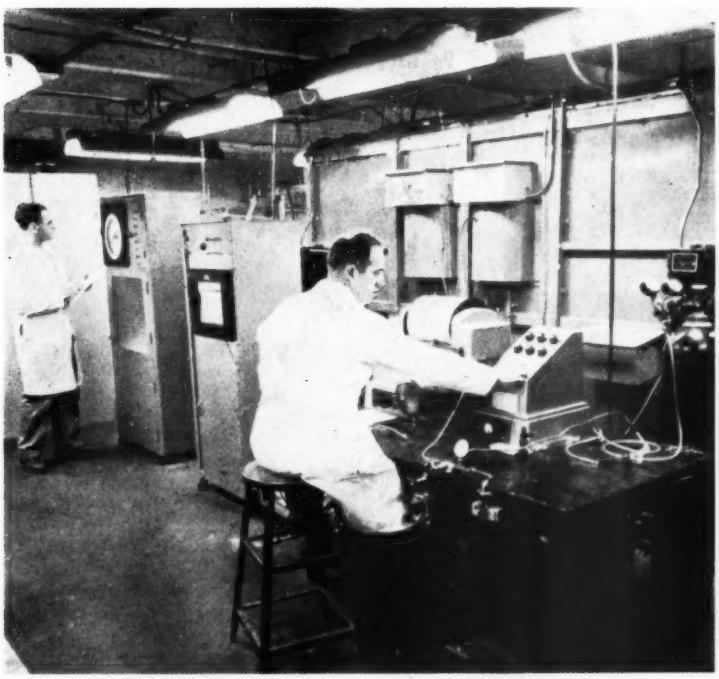

View of Air Mixture Treatment Chamber and Instruments.

(See Page 312)

February 1959
Vol. 8, No. 4

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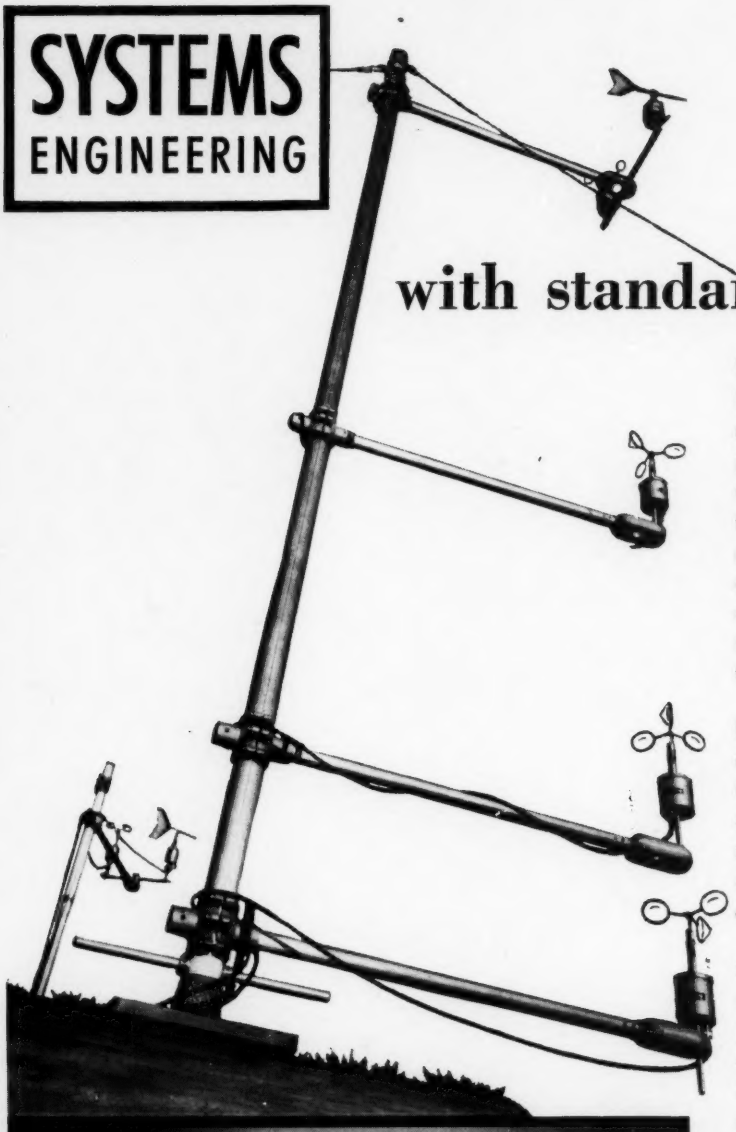

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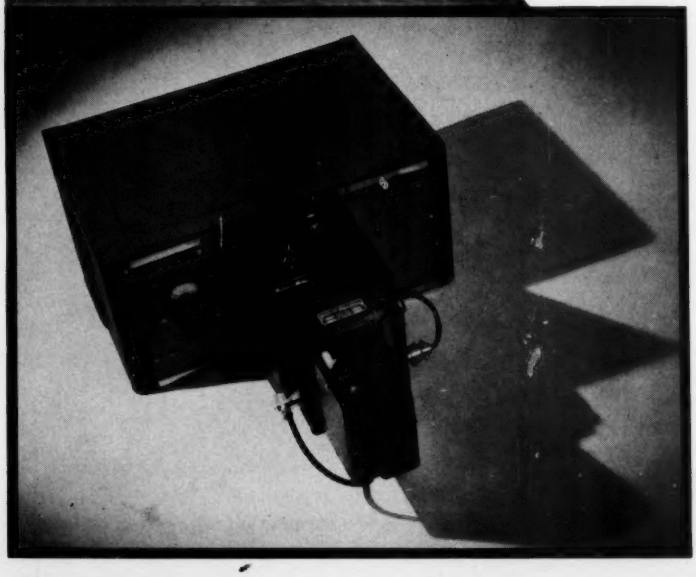

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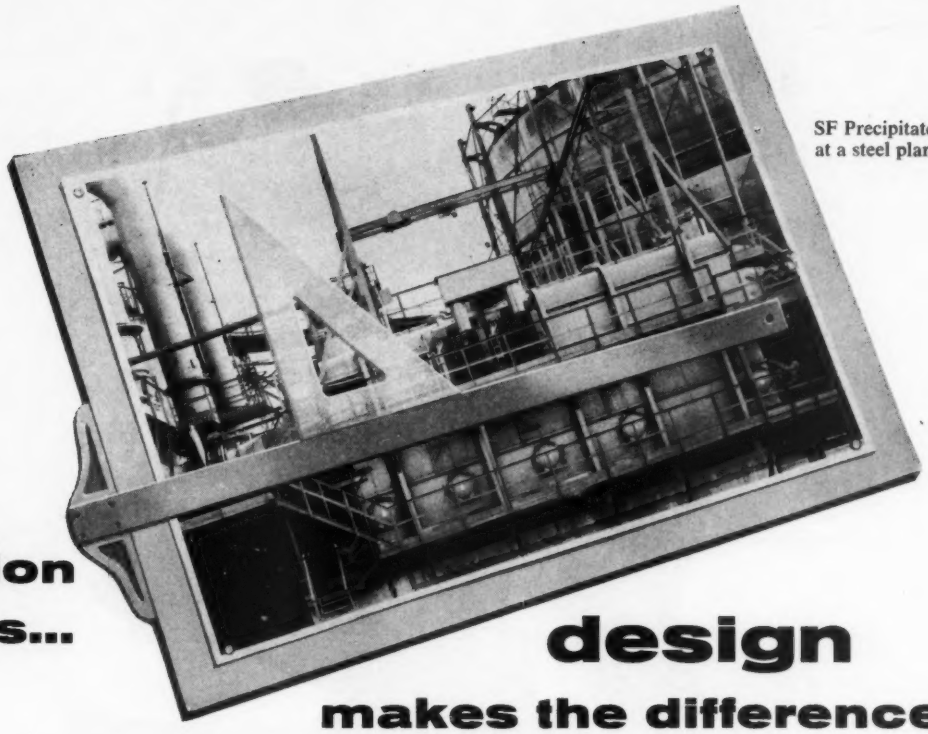

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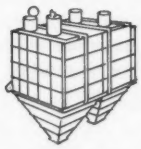

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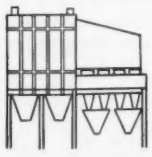

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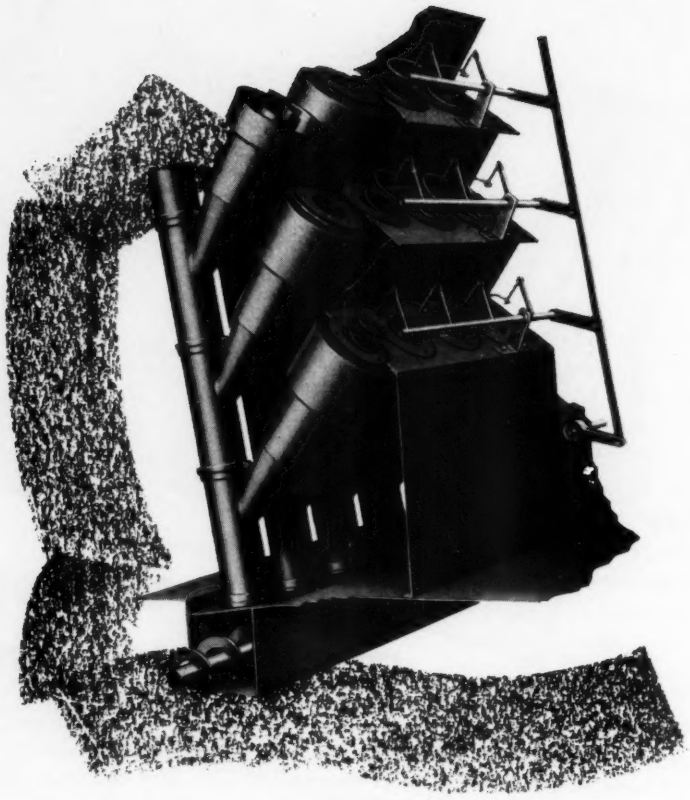

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JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

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Preliminary Design Investigation of CONTROLLED ENVIRONMENT SYSTEMS *for Air Pollution Studies*

H. BUCHBERG and **K. W. WILSON,** Department of Engineering, University of California, Los Angeles

A preliminary design investigation was undertaken to determine the necessary requirements and most functional, flexible, and economic arrangement of a controlled air environment system for air pollution studies that require duplication of the real air environment including photochemical reactions. The investigation included an evaluation of existing systems and new systems that have additional advantageous features, and an evaluation of materials that might be used in the construction of such systems. The evaluation of materials may be found in Reference 1 and will not be repeated here.

A system in which the natural air environment is simulated for the purpose of performing controlled experiments must have several features:

1. A temperature and humidity controlled clean air supply.
2. Pollutant generators to allow systematic pollution of the clean air.
3. A space in which the polluted air may undergo normal physical and chemical changes.
4. A test environment tailored to the requirements of particular experiments.

The composition of the clean air supply should approach the average composition of the earth's atmosphere. This is a large order unless small quantities of pure compounds can be blended and used. To be practical, it is necessary to specify the degree of air purity required in terms of maximum allowable concentrations of foreign substances. Pure air requirements will differ depending on the concentrations of contaminants desired in the polluted air stream. Obviously, the degree of air purity required for experiments in which normal atmospheric concentrations of contaminants are to be duplicated is much greater than if concentrations of perhaps 10 times normal amounts are desired. Consideration may be given to clean air sources derived by blending pure compounds, by bubbling atmospheric air through liquid air exchangers, by forcing atmospheric air through aerosol filters, chemical adsorbents, and a catalytic burner.

Depending on particular experiment requirements, pollutants might be introduced as pure compounds, as synthesized source effluents, or generated using real sources. In some instances known reaction products might be introduced initially as pollutants. A more detailed discussion of pollutant generators and entry controls may be found in Reference 2.

The natural air environment is highly reactive and its simulation usually requires the duplication of photochemical as well as dark reactions involving organic and inorganic substances. Reproduction of this dynamical system in a reaction chamber requires consideration of:

1. Solar irradiancy of the air mass and time of exposure
2. Spectral distribution of incident radiation
3. Concentration of pollutants at the point of introduction and subsequent mixing
4. Temperature
5. Humidity
6. Surface and wall effects
   - *a* Adsorption of gases on exposed surfaces
   - *b* Chemical reactions between surfaces and pollutants
   - *c* Chemical reactions catalyzed by surfaces
   - *d* Diffusion of gases through walls
7. Presence of aerosols
8. Air movement
9. Presence of vegetation, animals, and humans
10. Presence of biological agents such as fungi, bacteria, algae, and insects.

The space in which the polluted air is allowed to react initially may or may not be part of the test environment where experiments are actually performed depending on the size of the reaction chamber and the specific experiment to be performed. It is clear that the physical arrangement required for a test environment aside from the polluted air supply is different for animal toxicity and pathology studies, for studies of plant response, for the measurement of human visual performance, and for studies concerned with the deterioration of materials or changes in monomolecular protein layers similar to those occurring in the eye. This leads to the consideration of systems which would supply separate test environments such as plant fumigation chambers, animal fumigation chambers, human performance chambers in which visual, physical, and mental tasks are standardized.

Description of Controlled Air Environment Systems

There are several possible arrangements in which separate test environments may be supplied with air simulating the natural environment undergoing various kinds and degrees of pollution. Block diagrams of these systems are shown in Figs. 1, 2, 3, 4, and 5. Each arrangement has certain advantages and disadvantages which will be discussed in detail later. The designs of all of the reaction chambers shown in the various systems are based on the postulate that reaction times are relatively long. For short reaction times, of the order of seconds or less, simpler systems would suffice. Included in all of the systems, but not shown on the diagrams, are a number o

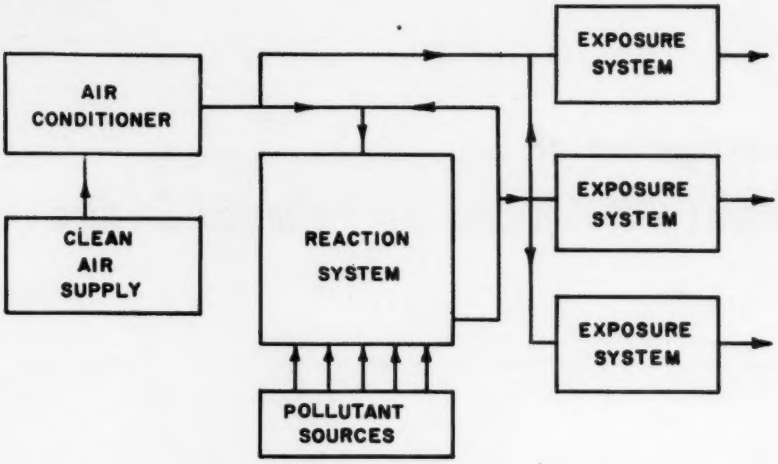

Fig. 1. Block diagram, controlled air environment System No. I.

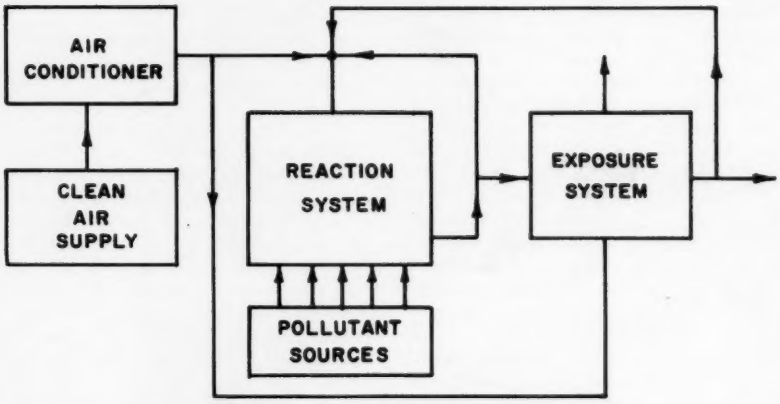

Fig. 2. Block diagram, controlled air environment System No. II.

exits appropriately placed, for continuous monitoring, intermittent sampling, and controls.

System No. I, shown in Fig. 1, comprises a conditioned clean air supply, appropriate source generators and influx controls, a cubical reaction chamber provided with a recirculating branch, and the necessary exposure chambers for specific experiments. Solar or artificial irradiation of the contents of the reaction chamber may be provided. The purpose of the recirculating branch is to keep the contents of the reaction chamber stirred in order to assure a homogeneous mixture and to prevent the settling out of aerosols. Perhaps the best example of this type of system is the Stanford Research Institute chamber[3] currently being used for eye irritation studies with automobile exhaust. In accordance with the block diagram shown, this system may be operated with or without recirculation and is ducted so that the exposure systems may receive alternately clean air or reacted polluted air.

System No. II, shown in Fig. 2, is essentially the same as System No. I except that a return duct is placed between the exposure and reaction systems providing for continuous recirculation with the necessary makeup.

System No. III, shown in Fig. 3, represents another approach in which the reaction and exposure spaces are combined allowing the atmospheric reactions resulting from pollution and irradiation to take place, from the beginning, in the presence of materials or subjects being exposed. This is schematically the same as the real system and may be accomplished in a large cubical type chamber, a natural bowl, or boxed-in canyon.

System No. IV, shown in Fig. 4, combines, to a certain extent, features of Systems I, II, and III. In this system a long reaction tunnel is arranged for once-through operation, recirculation through an exposure system, or recirculation through the reaction tunnel only. Removable exposure cells can be provided as part of the reaction tunnel itself. Pollutant sources may be introduced in one location or distributed along the reaction system in any manner desired.

A multiple-reaction chamber batch system is shown in Fig. 5 and designated as System No. V. This system may be described as a series of static reaction chambers which would be filled, irradiated, and their contents emptied into the exposure chamber in sequence continuously for the length of time required. After being emptied, each chamber would be refilled to undergo another cycle of operation.

The various systems described are not mutually exclusive. No one system can accomplish all purposes. Each has certain advantages and disadvantages that must be examined for a particular experimental program. Experiments in several different categories may be considered.

1 The determination of the effects resulting from the exposure of humans, animals, plants, and materials to an air environment polluted by different substances in various amounts.

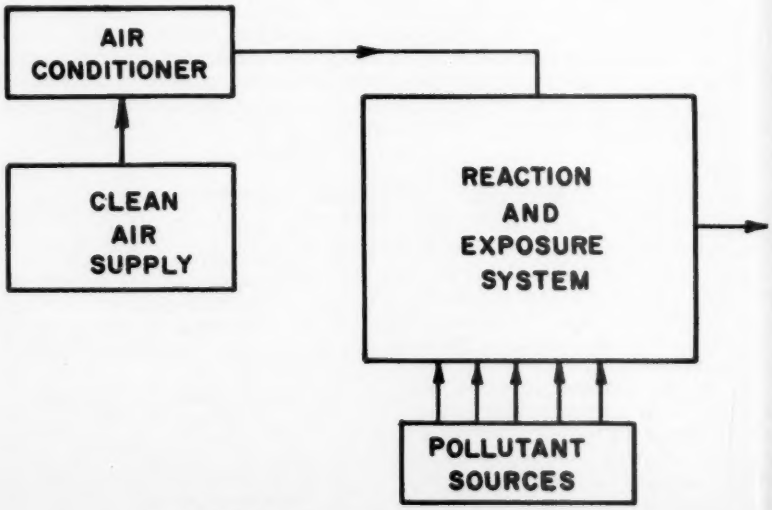

Fig. 3. Block diagram, controlled air environment System No. III.

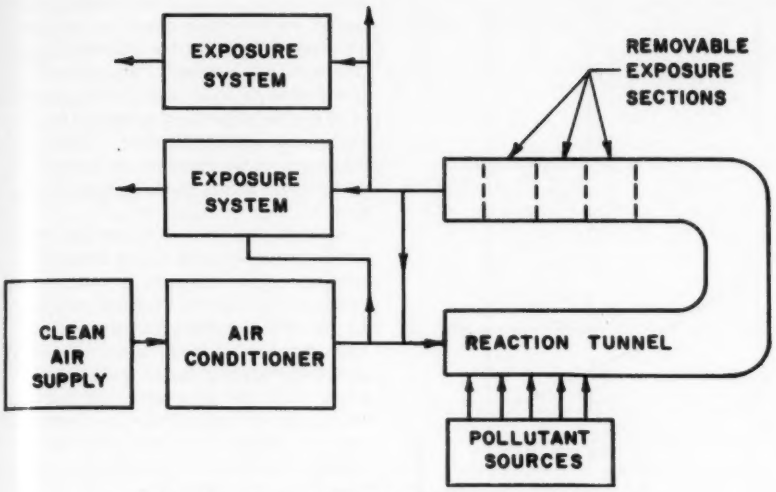

Fig. 4. Block diagram, controlled air environment System No. IV.

2 The identification of substances from various sources of pollution responsible directly or indirectly for various deleterious effects, and the amounts of these substances that must be removed to prevent or minimize these effects.

3 The evaluation of pollution control measures in terms of actual effects produced.

4 The investigation of reaction mechanisms in the polluted air environment.

Performance Characteristics

The performance characteristics of each of the systems described previously will now be considered.

The operation of System No. 1 (Fig. 1) initially requires thoroughly sweeping out the reaction and exposure chambers of old air (air present in the reaction chamber at the time exposure begins). Clean air and pollutants are then allowed to sweep through until the desired level of pollutants is attained. At this point the reaction system may be closed, irradiated, and recirculated for the length of time desired. Exposures may then begin by opening the appropriate inlet and exit valves while irradiation and recirulation are continued. Under these operating conditions, it is of interest to know the composition of the air used in the exposure studies in terms of the ratio of old air to new air (air entering reaction chamber after exposure begins).

Let

x = the flow rate of air drawn off for exposure tests
v = total volume of reaction chamber
a = quantity of new air in the reaction chamber at any time, θ (new air is defined as air entering reaction chamber after exposure test begins)
b = quantity of old air in the reaction chamber at any time, θ (old air is defined as air present in the reaction chamber at the time the exposure tests begin).

For a steady flow system,

a = new air introduced − new air exhausted

or,

$$a = x \cdot \theta - \int_0^\theta \frac{a}{v} x \, d\theta \qquad (1)$$

The solution for integrodifferential equation (1) is

$$\frac{a}{v} = 1 - e^{-(x/v)\theta} \qquad (2)$$

and,

$$\frac{b}{v} = e^{-(x/v)\theta} \qquad (3)$$

For example, if x = 20 cfm and v = 500

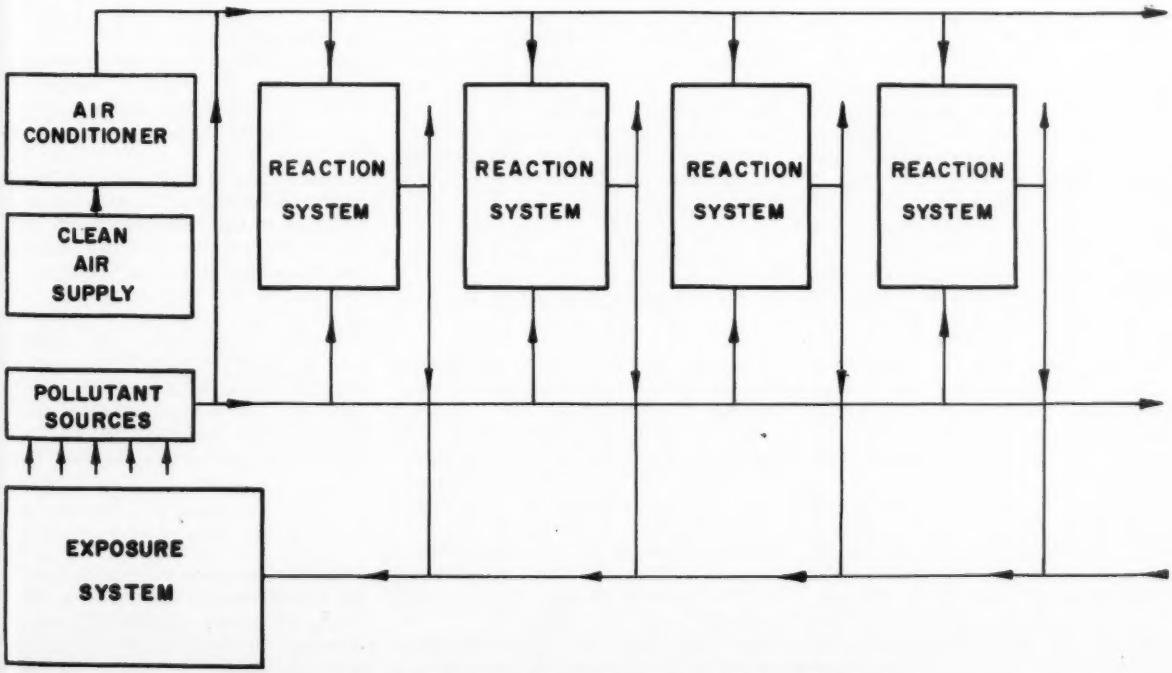

Fig. 5. Block diagram, controlled air environment System No. V.

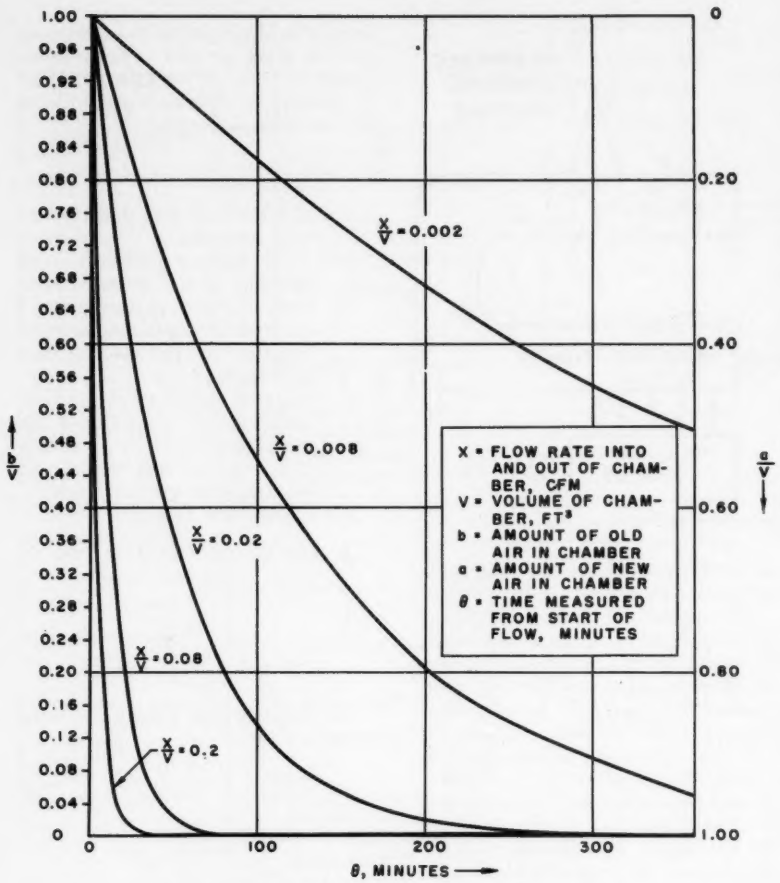

Fig. 6. Fraction of old or new air chamber at any time (θ).

ft³, only one-half of the air leaving the reaction chamber will be old air at the end of 17 minutes of exposure. The old air will have been irradiated an initial period plus 17 minutes, and the other half of the air supplied to the exposure chamber will be made up of parcels of air irradiated from zero to 17 minutes. If the volume of the chamber is increased tenfold, to 5000 cu ft, then it would take 170 minutes for the exit air to be one-half old air. After six hours of exposure, the air entering the exposure chamber would contain only 0.00008% old air (in the case of the 500 ft³ reaction chamber) and 24% old air (in the case of the 5000 ft³ reaction chamber). Obviously, the larger the volume (v) for a specified rate of flow, the smaller will be the value of x/v resulting in a larger fraction of old air making up the polluted reacted air supply for a given exposure test.

Equations (2) and (3) are interpreted graphically in Figs. 6, 7, 8 and 9. Figs. 6 and 7 present the fraction of new air (a/v) or old air (b/v) in the reaction chamber at any time (θ) for different values of the ratio, flow rate to total volume (x/v). From Figs. 8 and 9 one can obtain the age (irradiation time) distribution of the new air in the reaction chamber after one hour or six hours of exposure time. Curves of this type may be plotted easily for other exposure times. For a flow rate to total volume ratio (x/v) of 0.02 (this might be 10 cfm in a 500 ft³ chamber), we find from Fig. 6 that after one hour from the beginning of an exposure test, 70% is new air. This new air has an irradiation history as follows (Fig. 8):

0.6% of total vol. or 0.86% of new air was irradiated $\sim$ 60 min.
0.9% of total vol. or 1.29% of new air was irradiated $\sim$ 36 min.
1.8% of total vol. or 2.58% of new air was irradiated $\sim$ 4 min. (etc.)

System No. I may also be operated as a once-through system without recirculation; however, under such circumstances, when incomplete mixing obtains, it is not possible to predict the irradiation history of the air entering the exposure chamber at any time. Assuming that no mixing occurs, the residence time in the reaction chamber is given by the ratio of the total volume to the flow rate or v/x. For the first example used (v = 500 ft³, x = 20 cfm), the maximum residence time would be 25 minutes. In order to increase mean residence time in the reaction chamber, after an initial irradiation period recirculation could be stopped. Irradiated air could then be used until the new air reached the exit. Contamination of irradiated air by new air is, of course, dependent upon the mixing that occurs in the chamber. The cubical shape of the reaction chamber does not lend itself well to this type of operation.

Some discussion of temperature control in the reaction chamber might be of interest. The heat load is mainly the result of absorption of solar radiation by the walls and floor of the chamber and convection to the air. With the use of transparent walls and solar radiation, only the floor and recirculating duct can provide effective heat exchange surface without introducing additional surface. A considerable reduction in the load, when thin plastic film is used for the walls and roof, can be accomplished by making the floor transparent and in some manner removing the radiant energy transmitted through the floor (perhaps by a stream of water). Additional temperature control is obtained through control of the inlet air temperature. The inlet air may be subcooled to some extent to compensate for the chamber heat load.

With artificial radiation, the light sources may be built either into the walls of an opaque chamber or mounted outside of transparent walls. In the latter case the heat removal problem is similar to that for solar radiation. Some reduction in heat load can be accomplished by air blown over the lamps and chamber. If the lamps are mounted in the walls of the chamber, the heat removal problem is severe if anything approaching the intensity and spectral distribution of solar irradiation is achieved. If mercury arc lamps only are used, sufficient cooling may be obtained by means of an air blast over the lamps.

System No. II (Fig. 2) is similar in all details to System No. I except that it includes the necessary ducts and valves to return all or part of the reacted polluted air from the exit of the exposure chamber to the reaction chamber for recirculation. For some experiments this feature would reduce the required rate of flow of new air into the reaction chamber and increase the mean irradiation time for a given reaction space. If "n" represents the fraction of air returned to the reaction chamber, then

$$\frac{a}{v} = 1 - e^{-\frac{x(1-n)}{v}\theta} \qquad (4)$$

All of the discussion concerning System No. I applies to this system except when return air is used, equation (4) replaces equation (2) and the curves may be used keeping in mind that x/v is equal to x(1 − n)/v for this system. The

magnitude of fraction n will depend on the requirements of the subject undergoing exposure.

The essential feature of System No. III (Fig. 3) is the combined reaction and exposure space in which clean air is polluted by natural sources, irradiated, and allowed to undergo the reactions that normally occur in the real atmosphere. It is visualized that such a reaction and exposure system would accommodate motor vehicles, refuse incinerators, pilot process plants, and other pollutant sources; and vegetation, humans, and perhaps animals, all in their natural habitat. A large cubical chamber such as a blimp hanger or football stadium, a natural bowl, or a boxed-in canyon, might serve as the reaction and exposure system into which this microcosm is placed. Such a system would offer perhaps the closest approach to the real system (such as the Los Angeles basin) and yet be sufficiently small to make possible the performance of some controlled experiments.

It does not at this time appear feasible to attempt in a model system to duplicate the dispersion and dissipative patterns that exist in the real system as a result of meteorological, thermal, and topographical factors. Probably the best that can be done now is to start with a natural environment such as a boxed-in canyon and allow the diffusional processes to proceed naturally. The success of this approach depends primarily on the resulting rate of dissipation of pollutants within the test space. The residence time of a parcel of polluted air within the test space must be sufficiently long to allow reactions to take place as they would under conditions of inversion and low ventilation rates.

It is of interest to examine the relation between the pollutant volume fraction or concentration at any time, the ventilation rate, the pollution rate, and the total volume for an idealized system in which complete instantaneous mixing occurs. Let

ν_p = vol. fraction of pollutant at any time (θ)
$(\nu_p)_0$ = initial vol. fraction of pollutant
q_p = volumetric rate of pollution
q_v = volumetric rate of ventilation
v = total vol.

then, the increase in partial volume of the pollutant over a time interval ($d\theta$) is equal to the difference in volume entering and partial volume in the air leaving during the same time interval. Thus,

$$v d\nu_p = q_p d\theta - q_v \nu_p d\theta \qquad (5)$$

separating variables,

$$v \int_{(\nu_p)_0}^{\nu} \frac{d\nu_p}{q_p - \nu_p q_v} = \int_0^{\theta} d\theta \qquad (6)$$

and the volume fraction of pollutants at any time (θ) is

$$\nu_p = \frac{q_p}{q_v}\left[1 - e^{-\frac{qv\theta}{v}}\right] + (\nu_p)_0 e^{-\frac{qv\theta}{v}} \qquad (7)$$

If $(\nu_p)_0 = 0$,

$$\nu_p = \frac{q_p}{q_v}\left[1 - e^{-\frac{qv\theta}{v}}\right] \qquad (8)$$

For large values of θ,

$$\nu_p \cong \frac{q_p}{q_v} \qquad (9)$$

For one automobile, $q_p \cong 50$ cfm. If ν_p approaches $^1/_{1000}$, then from equation (10) we get $q_v \cong 50{,}000$ cfm. Let us now determine the volume required so that approximately 50% of the air present at zero time (after ν_p reaches $^1/_{1000}$) is still present after six hours. Fig. 2 indicates that for these conditions $q_v/v \cong 0.002$, or $v \cong 25{,}000{,}000$ ft³. This is about $^2/_3$ of the volume of the Los Angeles Coliseum. On the other hand, if the natural ventilation rate of the reaction space is about one mile per hour at right angles to a cross section of about 30,000 ft², $q_v = (30{,}000)$ 5,280/60 or 2,640,000 cfm. This would require a volume of about 1,320,000,000 ft³ for the reaction space and the continuous exhaust from about 53 automobiles. Actually, to determine the feasibility of a particular location, such as a canyon, from the standpoint of relative pollution and ventilation rates, it would be necessary to make a detailed survey over a period of time by means of smoke tests or tracer studies. Unless one were to provide a lid for the canyon, natural convection due to solar heating of the canyon walls might well be a serious difficulty.

In addition to the ventilation problem, it would be of interest to determine the order of magnitude of the heat removal problem. If a chamber about the size of the Los Angeles Coliseum (~40,000,000 ft³) was roofed with plastic film having transmission characteristics similar to polyethylene, the average heat load during the period between sunrise and sunset would be approximately 1×10^8 Btu/hr or about 10,000 tons of refrigeration. This could be reduced materially by painting all of the surfaces white. It would also be somewhat less due to the fact that the film transmits partially at long wave lengths. A panel cooling system behind all opaque surfaces that "see" solar

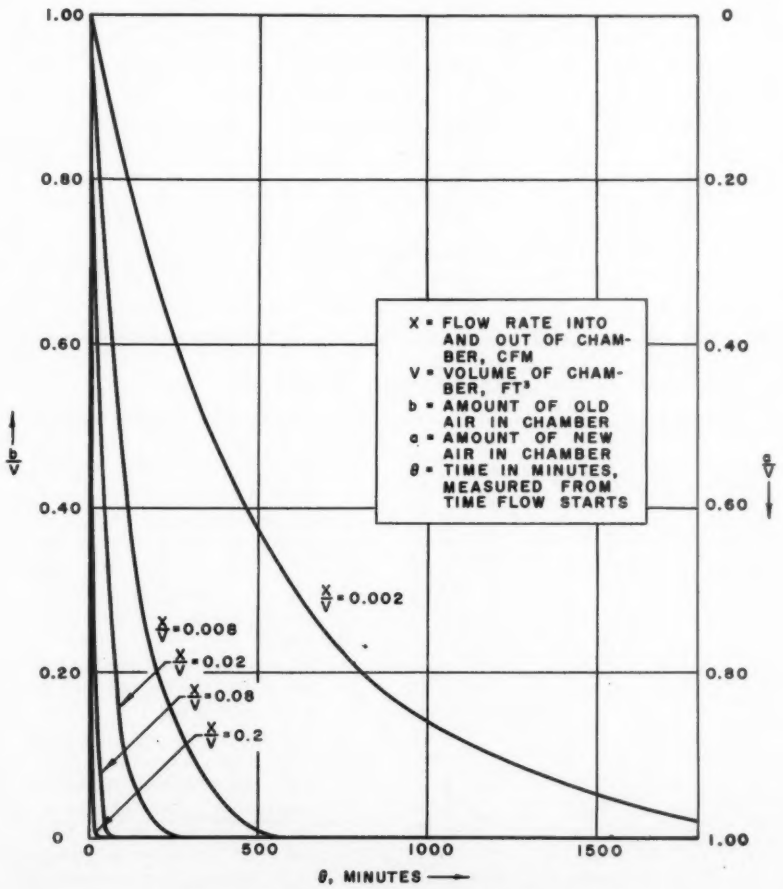

Fig. 7. Fraction of old or new air in chamber at any time (θ).

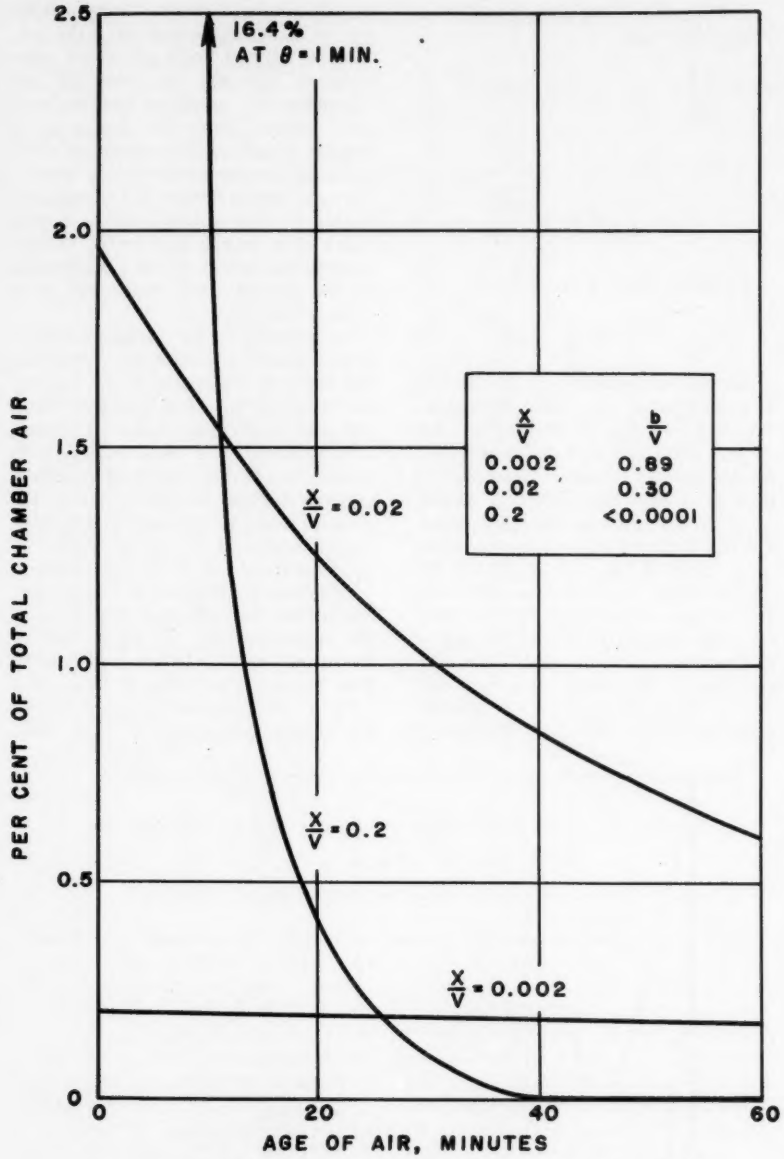

Fig. 8. Age distribution of new air at exit of reaction chamber after 60 minutes of flow.

radiation appears to be the most feasible method of removing the solar heat load.

System No. IV, shown schematically in Fig. 4, represents an attempt to combine some of the interesting features of Systems I, II, and III and to obtain additional features that may be advantageous. Operation of the system may be either once-through steady flow, recirculating steady flow, or return flow through an exposure system with or without tunnel recirculation. It is apparent that this system has the capability of separate and identical reaction and exposure spaces. The long path reaction tunnel has the following advantages:

1 The introduction of pollutants either at the entry or points distributed along the reaction space is more convenient.
2 Gas sampling and analysis at distributed points in the reaction system is more convenient.
3 A uniform distribution of pollutants can be obtained more easily.
4 Temperature and humidity control of the reacting air may be more convenient.
5 The tunnel shape lends itself better to an inexpensive pneumatic structure with the use of transparent plastic film covering and provides greater flexibility of size by increasing length through the addition of sections.
6 A circular tunnel cross section makes possible an almost constant irradiation path length through the entire air space.
7 The long tunnel-shaped chamber allows the removal of a greater volume of previously irradiated air without contamination of newly entering air for the same total volume of chamber.
8 Tunnel sections can conveniently be used as exposure chambers.
9 A circular tunnel cross section makes complete purging with clean air more effective.

When System No. IV (Fig. 4) is operated to supply an exposure chamber while air is recirculated at a high rate through the reaction tunnel, equations (2) and (3) may be used to describe the condition of the air entering the exposure system.

Consideration of System No. IV for continuous flow (i.e., without recirculation) is of interest. If the system is idealized, each parcel of clean air entering at one end is mixed with pollutants and travels along the tunnel maintaining its own identity while being irradiated and undergoing chemical changes. Assuming that slug flow pertained (each particle of air moving parallel to the axis of the tunnel with constant and uniform velocity) the distance along the length of the tunnel can be thought of as a time scale. Each point along the tunnel would represent a certain length of time, that time being the irradiation time for the air at that location. Thus, under these idealized conditions, air compositions resulting from various irradiation times up to the maximum would be available at points along the tunnel, and the supply of each particular mixture would be continuously available for analysis.

Two important idealizations have been implied for this system. One is that the irradiation is constant. This would be true for an artificial lighting system, but such a system would be exceedingly costly if the tunnel is long. The diurnal variation of solar radiation can be minimized considerably by use of a shutter scheme and floor surface treatments to give desirable radiation properties, but this would also be very costly for a long tunnel.

The second idealization is that slug flow, or uniform velocity profile conditions prevail. Even ideally, the profile would not be uniform; if the cross section were circular the profile would be parabolic for laminar flow, or as given by the $^1/_7$ power law for turbulent flow. For a semi-circular cross section, these profiles would be modified. Two additional difficulties of a more serious nature arise: turbulent diffusion (molec-

ular diffusion is negligible by comparison) superimposed on the mean flow, and the breakdown of the whole flow pattern due to thermal gradients. Inasmuch as the system is inherently nonisothermal, some turbulent convection will take place even if forced flow is maintained throughout the tunnel. To the extent that the mixing is radial, convection is a desirable feature since it will assure homogeneity over the cross section. Axial diffusion, which is always present and may even be the major component, has the effect of spreading out the parcels of air irregularly so that they partly or completely lose their identity as they travel down the tunnel. If the mean forced flow velocity is made to be appreciably greater than the diffusion rate, some lessening of this effect may result. However, if the residence time is unchanged (by increasing the tunnel length) the increased mean flow velocity may not help unless one considers the individual air parcels to be correspondingly increased in length or unless the increased velocity eliminates the diffusion velocities. Experiments have been conducted to determine typical diffusion rates in still air under conditions approximating those of the tunnel. These experiments were discussed in Reference 2, but the main result of those tests is that typical diffusion velocities in still air, as determined by the time taken for an identifiable air parcel to travel 48 ft, is about 10 ft/min. The mean forced flow velocity through the tunnel must be enough greater than this to eliminate the diffusion components if the validity of the scheme of stretching out the reactions along the length of the tunnel is to be preserved. This would require a tunnel about one mile long for reasonable residence times, which is impracticable at the present time.

System No. V (Fig. 5) may be thought of as a multiple chamber system or batch process. If the previous idealized tunnel with slug flow is imagined to have many impenetrable barriers it becomes a system of separate cells, each containing a single parcel of air. Each cell requires inlet and outlet ports, valves, and perhaps an internal mixing device. The train of cells may be imagined to pass the inlet air and pollutant supply depot to be filled in turn with similar material, or we may think of a stationary system with appropriate manifolds and valves as shown in the schematic diagram of Fig. 5. If the cells are filled, irradiated, and emptied in sequence, the system will approximate idealized slug flow. As the number of cells increases, the size of each decreases, and the length of time each cell spends at the filling depot decreases. The batch system approaches the continuous slug flow system as the number of cells increases. If the residence time is made to be six hours in the continuous flow tunnel, $^1/_{72}$ of the total length would be the distance of travel of the air mass in five minutes and would represent five minutes of irradiation time. If that volume of air is considered as one homogeneous parcel of air, then a series of 72 cells, each of that same volume, would be equivalent to the slug flow system. The cells would be filled at the filling depot at five-minute intervals; any sampling to be done would require drawing off samples during five-minute intervals from the cells in proper sequence. The air sent to the exposure chambers would also be drawn off during five-minute intervals. Thus, assuming zero time for valve switching between cells, the air drawn off in this manner would be a continuous supply of air of a specified age within $\pm 2^1/_2$ minutes. Since each box is a static system the problems arising with the previous system, with its gross deviations from the idealized slug flow, are eliminated. Convection currents within each box cause no difficulty and even aid in the now desirable mixing process.

The major difficulties with this batch system are mechanical, having to do with emptying the cells. Since there is no continuous flow through the cells to move the air, other more involved air handling techniques are required. Evacuating the chamber to be filled by the air from the cells is obviously one solution and, for the case of removing air samples for analysis, a simple and acceptable one. For the final emptying of the cells, vacuum techniques will probably not be acceptable. Either a piston arrangement or a collapsing cell would serve to drive the air out. The collapsing container problem has been studied in connection with collapsible Kel-F rocket propellant bags, but the relatively large size of the reaction cells and the high number of collapsing cycles make the problem very much more severe in the present application. A piston design, on the other hand, appears to offer a possible solution. A piston made of glass sheet (for trans-

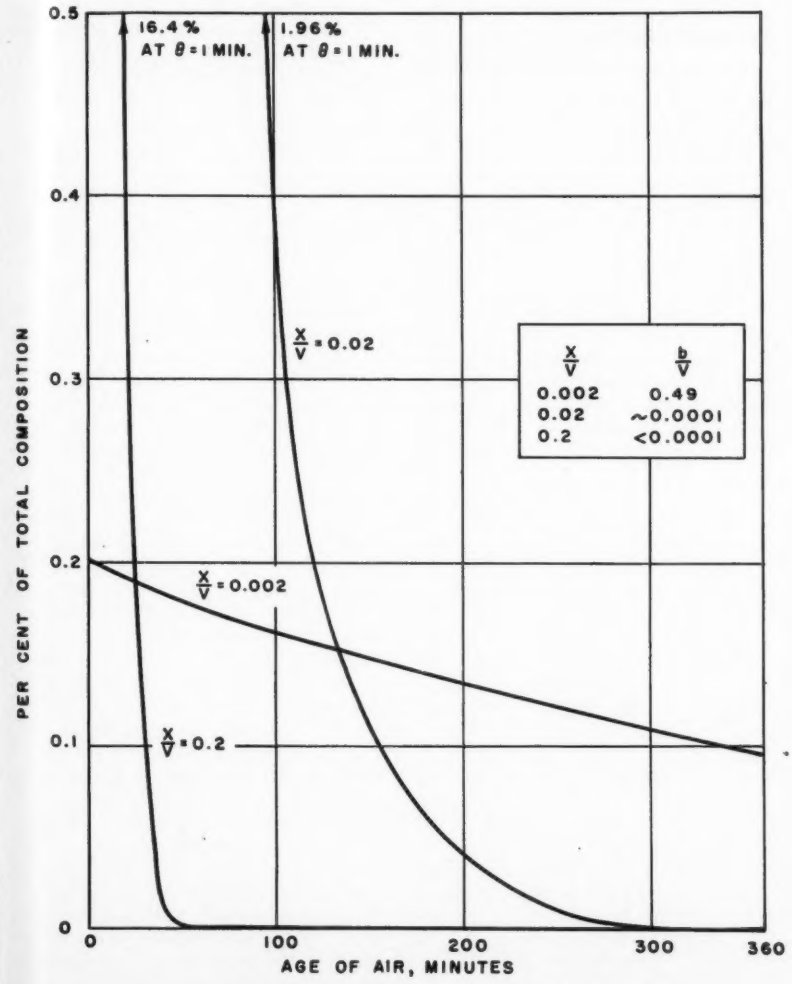

Fig. 9. Age distribution of new air at exit of reaction chamber after 360 minutes of flow.

parency, inertness, and rigidity) equal in area to one side of a rectangular box (or one end of a cylindrical-shaped chamber) and driven by a piston rod, would serve to drive the air out of the cell. A good seal between the piston and the flexible plastic sides of the cell would not be required. If, for example, 10% of the air leaked past the piston as it was driving out the air, the cell would be made enough larger so that the required quantity of air would be transferred to the exposure chamber. A sufficiently adequate seal for the piston rod should present no great problem.

The initial filling of each cell cannot be accomplished conveniently with the piston because appreciable amounts of contaminated air would remain. Filling can also be accomplished by sweeping the cell with clean air to remove contaminated air, closing the cell, then introducing the small quantities of pollutants as required. Once a cell reaches the end of the irradiation cycle and discharges its contents it can be swept out with clean air to start again.

Conclusions

As a result of these studies it was concluded that, for air pollution studies which require the duplication of the natural air environment including photochemical effects, System No. IV was the most promising. System No. IV appears to offer the greatest flexibility in the performance of experiments in the categories listed previously with the possible exception of some investigations of reaction mechanisms where smaller more convenient systems subject to better control of irradiation would be more desirable. System No. IV also offers economy, particularly for experiments which can tolerate a polyethylene air reaction tunnel[1] and for experiments designed to further elucidate design factors concerned with the duplication of the natural air environment.

A controlled air environment system similar to No. IV utilizing a polyethylene reaction tunnel has been constructed. It has been used successfully to produce smog (Los Angeles variety) in preliminary tests. A description of the design and performance characteristics is given in Reference 4.

Acknowledgments

The studies presented are part of a continuing investigation of air pollution problems being conducted by the Department of Engineering, University of California, Los Angeles, and supported by the State of California.

The authors gratefully acknowledge the assistance of R. P. Lipkis in much of the early work connected with this project.

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The Chemical NATURE *of the* PARTICULATE *in Irradiated* AUTOMOBILE EXHAUST

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G. J. DOYLE, Stanford Research Institute, Menlo Park, California

The Los Angeles smog is characterized by its several manifestations namely, eye irritation, crop damage, reduced visibility, and high ozone concentrations. Since automobile exhaust is the major contributor to the pollution of the Los Angeles atmosphere we are studying its relation to all aspects of smog formation. Previous work[1,2] has shown that the irradiation of dilute auto exhaust (2550 ppm by vol. in purified air) produces large numbers of particles in the size range 0.2–0.5 μ diameter. Furthermore, it has been estimated that such particulate concentration could cause serious reduction in visibility comparable to that occurring in smog.[3]

There have been three studies of the chemical nature of the particulate in non-irradiated auto exhaust from several cars reported previously.

Hirschler, et al.,[4] made a comprehensive study of the amount, composition, and particle size distribution of the lead compounds in the exhaust gases from automobile engines burning leaded fuel. They showed that the lead particles are mainly of the form $PbCl \cdot Br$, α and β forms of $NH_4Cl \cdot 2PbCl \cdot Br$, and $2NH_4Cl \cdot PbCl \cdot Br$. They report that 5 percent by weight of the particles are in the size range 0 to 1 μ diameter.

Gates[5] collected samples of auto exhaust particulate directly using an electrostatic precipitator. His analyses indicated that the material contained compounds of high molecular weight. Some of these were aldehydes. The particles after they were once formed were not volatile and were only slightly hygroscopic. Oxidants and strong organic acids or bases were absent.

McKee[6] collected samples of particulate on glass fiber filters and analyzed the benzene soluble organic fractions. He reports the presence of carbonyl compounds in contrast to its absence in the lubricating oil as well as compounds with aliphatic unsaturation. Pyrene was identified and other fluorescent traces indicate the presence of other polynuclear aromatic compounds.

There appear to be no reports on the nature of photochemically generated aerosol in auto exhaust.

Apparatus and Materials of Research

The laboratory facility used in this work has been described previously[7] (see Figs. 1–5). During the collection of the photochemically produced particulate samples, a filter was placed in the inlet line to the irradiation chamber as shown in Fig. 1. Its purpose was to remove most of the particles which would otherwise contribute material of non-photochemical origin to the collected sample. Tests with the O'Konski light scattering counter photometer and the Goetz aerosol spectrometer showed that up to 90 percent of the exhaust particulate was removed. In spite of this, the aerosol level, due to photochemical generation finally achieved in the test chamber, was comparable to the non-filtered situation, although it was produced at a slower rate.

The inlet filter consisted of two truncated galvanized sheet steel cones fitted together by short overlapping cylindrical sections at their bases. The resulting seam was taped to stop leakage. An interior flange within one of the cylindrical sections served as a filter mount. Three layers of Mine Safety Appliances (MSA) 1106 flash-fired glass mat filters[8] were clamped between the support rings of a backing screen and the flange by means of studs and wing mats (see Fig. 2). The effective diameter of the filter area is about two feet.

When collecting photochemically produced aerosol material the entire flow through the irradiation chamber was drawn through a single layer of MSA 1106 glass mat filter for several hours by means of a Staplex high volume

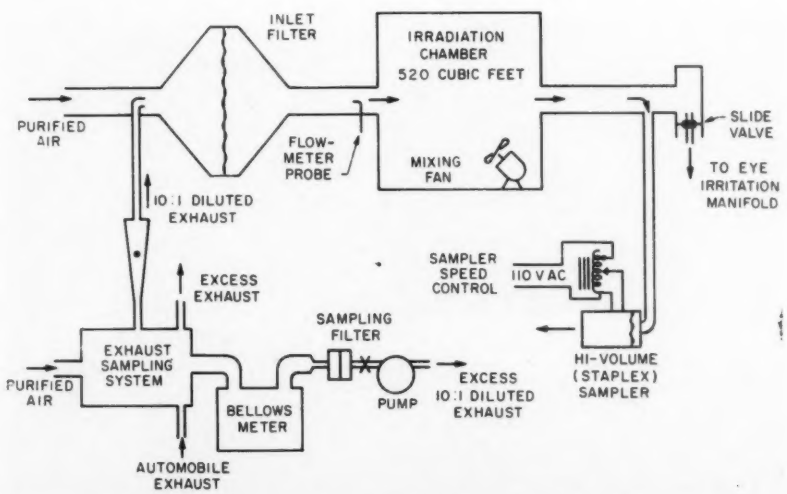

Fig. 1. Schematic diagram showing location of inlet filter and sampling filters.

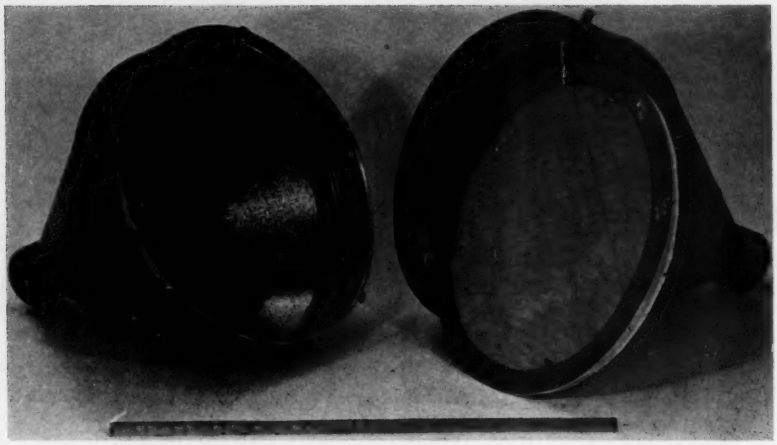

Fig. 2. Inlet filter.

Fig. 3. Photochemical aerosol sampling filter.

Fig. 4. Auto exhaust sampling filter.

sampler. A simple adapter was used to attach the sampler to a 3-in. sheet steel pipe at the chamber outlet as shown diagrammatically in Fig. 1. A photograph of the disassembled sampling arrangement is shown in Fig. 3. The sampling rate was adjusted to match the chamber flow by means of a variable auto transformer. The diameter of the effective filter area was 3.54 in.

Samples of aerosol material in 10:1 diluted auto exhaust (see Fig. 1) were taken. Collection of the material emitted from a dry gas meter in the exhaust line for excess 10:1 mixture was carried out for several hours. The sampling arrangement consisted of a single layer of MSA 1106 glass fiber filter in a filter holder and a pump which was throttled to adjust the flow. The filter holder consists of two accurately machined cylindrical brass pieces, one of which fits inside and presses the filter pad against an interior shoulder and backing screen inside the other piece. An O-ring gasket around the outside of the interior piece secures against leakage. The two pieces are held together by means of a knurled collar working against a shoulder on the interior piece and threaded to the exterior piece. A photograph of the disassembled holder is shown in Fig. 4. The test car was a 1954 Dodge and the exhaust gas was a mixture of the four cycles of driving in the volume ratio 1:7:18:9 (idle, accelerate, cruise, decelerate).

Experimental Design

All of the aerosol collected for the chemical analyses was generated under similar conditions. The irradiated chamber was first flushed with pure air and then auto exhaust at 5000 or 7200 ppm by volume was allowed to enter the chamber, after passing through the inlet filter. As soon as steady state concentrations were reached, the chamber irradiation lamps were turned on. The experiments were dynamic in nature with 1-hr residence time for the mixture in the chamber during which period the irradiation took place. The aerosol under study was that generated essentially in a stirred flow reactor. The runs lasted up to 9 hr in order to collect samples of sufficient size for the standard microanalytical techniques to be used in the analyses.

Results

The first runs were made at 5000 ppm auto exhaust and the collected samples were used for exploratory chemical analyses of a qualitative nature. Two samples, one analyzed by the Menlo Park Laboratory of Stanford Research Institute using the microcombustion technique and one by the Chaney Laboratories using standard

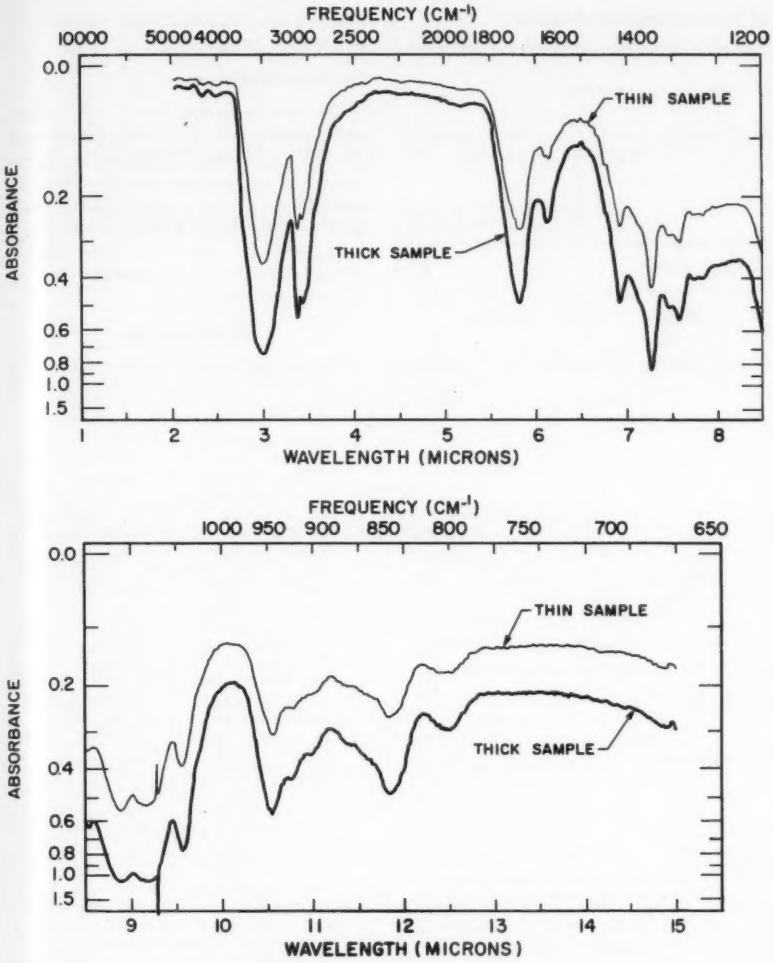

Fig. 5. Infrared spectra of ether extract of an aerosol sample.

microanalytical chemical techniques gave the results shown in Table I.

The material is seen to consist mostly of carbon, hydrogen, and oxygen with traces of other materials, chiefly nitrogen. The material is highly oxygenated. The infrared spectra (Fig. 5) definitely indicated the presence of hydroxyl and carbonyl groups which are probably aldehydic. An example of the many compounds which fit these specifications approximately is glyceraldehyde, $C_3H_6O_3$.

Spectra

A sample of the material consisting of 36.3 mg of the material was analyzed by Truesdail Laboratories. They extracted for 16 hr with 5 ml of ethyl ether in a Soxhlet extractor. Spectral transmittances of the ether solutions were measured in the visible and ultraviolet regions (Fig. 6).

A second sample was sent to the Menlo Park Laboratories of Stanford Research Institute. This consisted of 66.5 mg of material which was extracted for 72 hr with a small amount of ethyl ether. The viscous syrup produced by evaporation was placed between plates and the infrared absorption spectrum was measured (Fig. 5).

The strong absorption which begins in the visible and becomes stronger as the wave length decreases into the ultraviolet is the most salient feature of the short wave spectrum (Fig. 6). This is not very useful for chemical identification although it does eliminate from consideration large classes of compounds such as paraffinic hydrocarbons which were already eliminated for other reasons. However, it does have interesting implications for the optical properties of aerosols of this material. The material will probably have a strong dispersion, the index of refraction increasing toward the ultraviolet indicating that blue and ultraviolet light will be scattered more than longer wave lengths. Absorption at these wave lengths has to be very strong before this will greatly affect the scattering properties directly. However, multiple scattering in thick clouds of aerosol can lead to attenuation in the blue end of the visible spectrum.

Two samples each of dilute auto exhaust—unirradiated (at 1 to 10 dilution), and irradiated at 7200 parts per million—were collected and analyzed by the Chaney Laboratories. The results are shown in Table II which also includes smog sample analyses. The data for the unirradiated exhaust at 1 to 10 dilution were adjusted to the more comparable atmospheric dilution, such as used in the irradiated case.

Briefly, the methods of analyses were as follows:

Nitrate — phenoldisulfonic acid reagent

Sulfate—turbidimetric as barium sulfate stabilized with propylene glycol and alcohol

Lead—acid digest, dithizone at pH 8.5

Water Soluble Organic—change in optical density at 580 mμ of acidic dichromate solution due to reduction by compounds soluble in water

Ether Soluble—weight loss due to ether extraction

Ammonia—Conway microdiffusion

The most interesting features of these data are the values for nitrate and sulfate which are formed in the chamber. It is thought that the nitrate is a consequence of the photochemical processes during which NO and NO_2 are oxidized. It appears further that the sulfate must result from the oxidation of SO_2, either in some direct photochemical way or as a result of secondary reactions. However, this matter is obscure since we have

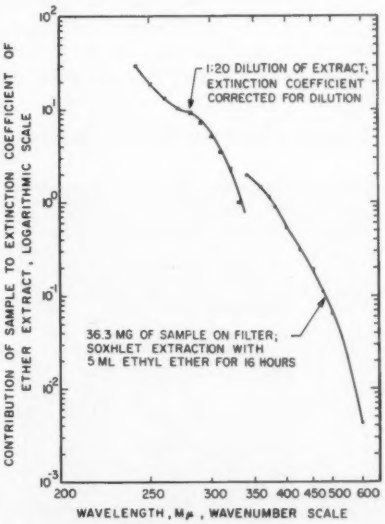
CONTRIBUTION OF SAMPLE TO EXTINCTION COEFFICIENT OF ETHER EXTRACT, LOGARITHMIC SCALE
1:20 DILUTION OF EXTRACT; EXTINCTION COEFFICIENT CORRECTED FOR DILUTION
36.3 MG OF SAMPLE ON FILTER; SOXHLET EXTRACTION WITH 5 ML ETHYL ETHER FOR 16 HOURS
200 250 300 350 400 450 500 600
WAVELENGTH, Mμ, WAVENUMBER SCALE

Fig. 6. Contribution of dissolved material to extinction coefficient of an ethyl ether extract of an aerosol sample as a function of wavelength.

Table I—Results of Analyses of Photochemical Aerosol

Atomic Species	Elemental Analysis, wt-%	Atomic, %[b]
C	34.0	23.8
H	5.3	44.2
N	1.8	1.1
O[a]	59	31

Auxiliary Analyses and Trace Species

Analysis for	Method	Weight, %	Atomic, %
N	Phenoldisulfonic acid (NO_3^-)	0.6[3]	0.3[7]
N	Conway micro-diffusion (NH_3)	1.4[3]	0.8[8]
Cations			
Na		<1.0	<0.3[6]
K		<0.2	<0.04
Ca		<0.5	<0.1
Fe		Neg.	Neg.
Pb		0.2	0.008

[a] Oxygen was estimated by difference assuming C, H, N, and O to be the major contributors to the sample weight.
[b] Percent of all atoms contributed by a particular species.

no data on SO_2 concentrations in our system.

The presence of ammonia in the original exhaust is consistent with Hirschler's study.[4] However, we find an increase in this component in the chamber which suggests some reactions taking place not previously hypothesized.

The presence of considerable quantities of water and ether soluble organics is consistent with the observations of others.[9, 10]

A comparison of Tables I and II suggest that the material not accounted for in Table II is composed of high molecular weight organic compounds.

Conclusions

Irradiated auto exhaust appears to be the principal source of nitrate, sulfate, lead, and organic compounds in the particulate matter of Los Angeles smog. Further, these findings explain the higher values of nitrate and sulfate found in Los Angeles and other similar West Coast cities in comparison with other cities (see Ref. 11).

If we assume six million gallons of gasoline are consumed in auto engines per day in Los Angeles, we compute from our data that about one ton per day of non-irradiated particulate and at least 10 tons per day of photochemically generated particulate are present in a typical smog.

Table II—Concentration of Components of Particulate Micrograms per Cubic Meter

Component	In Irradiated Auto Exhaust at 4000 ppm Fuel A	Fuel B	In Unirradiated Auto Exhaust at 4000 ppm Fuel A	Fuel B	Smog[a] Average	Range: Min.	Max.
Total Particulate →	370	340	45	Not available	383	145	760
Nitrate (NO_3^-)	38	32	0.1	0.0	24	1	116
Sulfate ($SO_4^=$)	31	20	2.3	0.0	27	1	150
Lead (Pb)	1	2	10	8	7	1	16
Water soluble organic	90	48	1.8	<0.7	—		—
Ether soluble organic	156	185	4.5	24	70[b]	5	250[b]
Ammonia	4	3	0.1	0.02	—		—

[a] Renzetti, N. A., "An Aerometric Survey of the Los Angeles Basin, August–November, 1954," Air Pollution Foundation Report No. 9, July, 1955.
[b] Benzol soluble. Fuel A, 0.22% sulfur. Fuel B, 0.08% sulfur.

Acknowledgment

We are indebted to E. A. Schuck and Roger Lewis of Stanford Research Institute, South Pasadena, for the operation of the basic facility and its associated instrumentation and to the analytical group of the Menlo Park Laboratories of Stanford Research Institute for the interpretation of the infrared spectra.

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Air Pollution EFFECTS *of Incinerator* FIRING PRACTICES *and Combustion* AIR DISTRIBUTION

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Atmospheric pollutants produced from the incineration of municipal and industrial refuse include solid, liquid, and gaseous compounds formed by the volatilization, destructive distillation, or incomplete combustion of the various components. Through proper incinerator design and operation it should be possible to reduce discharge of these contaminants to the atmosphere. At present there is a lack of generally accepted incinerator design standards and of criteria for minimizing discharge of atmospheric pollutants. Similarly there are no generally accepted firing practices for incinerators.

To more rapidly develop these standards and criteria, the U. S. Bureau of Mines is studying the single chamber incinerator at the same time that the Public Health Service is studying the multiple chamber type.

This report covers the first phase of the multiple-chamber incinerator study, which was to obtain, on a test incinerator of fixed dimensions, information on the effect of varying (1) amount and distribution of combustion air, (2) burning rate as measured by the amount of fuel charged per hour, (3) amount of fuel per charge, and (4) the interval between stoking* the burning fuel bed. Later studies will be concerned with effects of varying dimensions, velocities, and temperature gradient.

Experimental Incinerator

A small, refractory-lined, multiple-chamber prototype incinerator was constructed (Fig. 1) based on the relationships proposed by Rose and Crabaugh.[1] The primary combustion chamber has a length-to-width ratio of 2, and a grate area of 8.5 sq ft. Volume ratio of the primary to final combustion chambers is 1.06. The elliptical arch was designed to concentrate heat developed in the ignition (primary combustion) chamber onto the front third of the grate for more rapid ignition of incoming fuel. The front two-thirds of the grate slopes 30° from the charging door to a horizontal dumping grate at the rear of the ignition chamber. Fuel is charged through a front-opening, guillotine-type door. The unit is built in sections formed by pouring four inches of high temperature, castable refractory onto sheet steel frames. These sections are bolted together and can be easily disassembled to permit changing physical dimensions with a minimum of new construction.

The present arrangement employs an in-line design with a down-pass mixing chamber located immediately behind the ignition chamber. The mixing chamber is followed by the final combustion or expansion chamber (Fig. 2). Combustion gases from the ignition chamber pass through a high velocity throat over the bridge wall, travel downward through the mixing chamber, and horizontally under a curtain wall to enter the bottom of the final combustion chamber. These gases then travel upward to discharge at the top of this chamber through a short breeching into the stack.

Combustion Air

Overfire combustion air is introduced into the front of the ignition chamber, under the charging door, at the grate level, and sweeps the surface of the burning fuel bed. Underfire air enters through the ash pit and passes up through the fuel bed. Secondary air is introduced through a duct built into the top of the bridge wall and discharges through a series of ports opening into the top of the mixing chamber. All combustion air entries are fitted with calibrated ducts to permit control and measurement of the air flow supplied at each point (Fig. 3). Thermal anemometers mounted inside each duct meter the flow separately for primary overfire, primary underfire, and secondary air. Strip-chart millivolt recorders measure and record the electrical output of the thermal anemometers, indicating the instantaneous flow rate and providing a permanent record of total combustion air flow (Fig. 4).

Fuel

In order to correlate results from this multiple-chamber incinerator study with results from the single-chamber study of the Bureau of Mines, fuel of essentially the same composition is being used in both studies. It was necessary to select a fuel (1) readily available at both study sites and (2) of such composition that contaminant responses would reflect changes in design parameters and operating conditions. The fuel selected consists of newspaper, corrugated cardboard, wood, and leafy vegetables (Fig. 5). Equal parts, by weight, of newspaper and cardboard comprise the paper component which is mixed in a ratio of 3 to 1 with wood chips. On the basis of a standard toluene-extraction method for

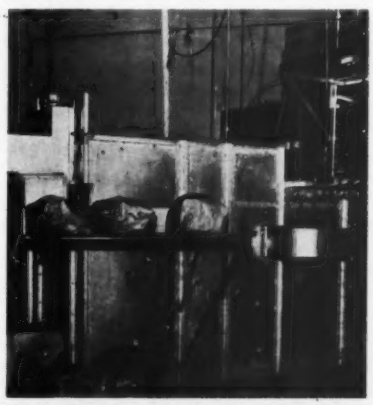

Fig. 1. Experimental multiple chamber incinerator.

* Stoking refers to stirring of the entire fuel bed.

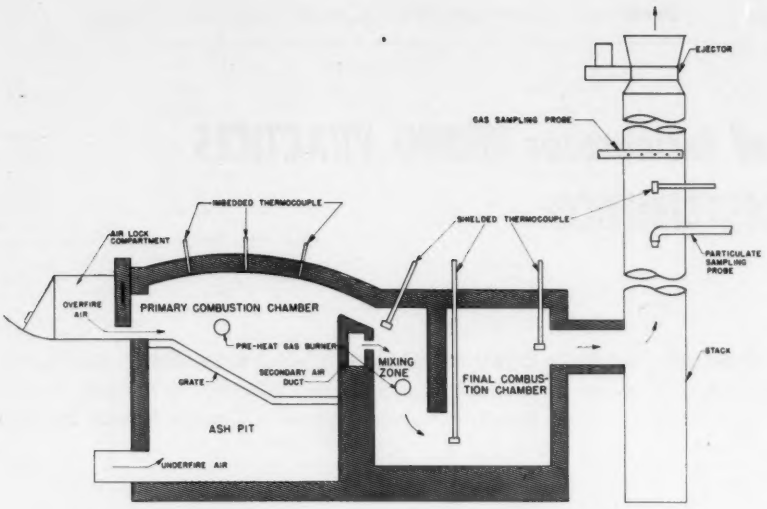

Fig. 2. Schematic elevation of experimental multiple chamber incinerator.

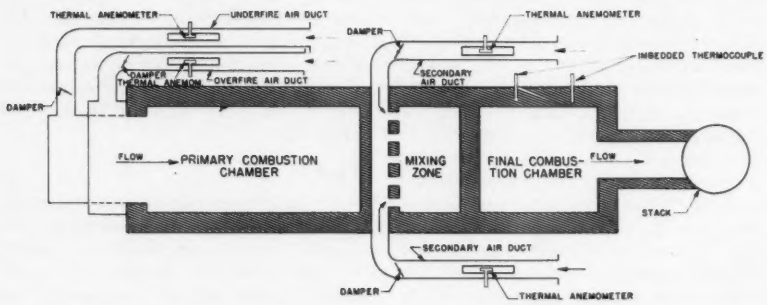

Fig. 3. Schematic plan of experimental incinerator showing air-metering ducts.

determining moisture content, wet leafy vegetables—predominantly lettuce, cabbage, and kale—are added in sufficient quantities to raise the moisture content of the average fuel mixture to 25%. Newspaper and cardboard are cut in 4-in. squares, and the newspaper is left in compact stacks. The wood component consists of chips about $^1/_4$ x $^1/_2$ x 2 in.

To facilitate charging the incinerator with accurate quantities of fuel, charges were prepared in advance of burning by weighing proportionate amounts of each material in paper sacks (Fig. 6). A sack containing a 5-lb. charge of fuel with a moisture content ranging from 23% to 27% consisted of $1^1/_2$ lb of newspaper, $1^1/_2$ lb of cardboard, 1 lb of wood, and 1 lb of wet vegetables.

All tests in this study involved 25 percent moisture content fuel. Future tests will be made employing fuels of up to 50 percent moisture content.

Sampling and Instrumentation

Evaluation of effects produced by experimental variables is dependent on collection, sampling, and analysis of both solid and gaseous contaminants. Automatic instrumentation was used where feasible to reduce manpower requirements and to obtain continuous records of instantaneous concentrations of certain pollutants (Fig. 7).

Oxygen and carbon dioxide content of the flue gases was continuously measured and recorded, using analyzers employing principles based on the paramagnetic properties of oxygen and the thermal conductivity of gases (Fig. 8). Carbon monoxide content was measured by passing a continuous stream of effluent gas through a positive type non-dispersive infrared gas analyzer, employing a diaphragm cell, with a range from 0 to 5% and operating at a wave length of 4.4 μ. Hydrocarbon concentrations of the flue gases were monitored by a positive type infrared gas analyzer sensitized with hexane and operating at a wave length of 3.4 μ with a range from 0 to 750 ppm (expressed as hexane). Oxides of nitrogen, expressed as NO_2, were determined by the Griess colorimetric method as modified by Saltzman.[3] For this determination grab samples of the flue gases were collected in evacuated flasks containing Saltzman reagent.

Particulates in the flue gas were sampled isokinetically at a representative point (Fig. 9) eight diameters downstream from the breeching and eight diameters upstream from the top of the stack. Solids were collected on an MSA type 1106-BH glass-fiber filter without organic binder. Mass determination of the solids was made on an analytical balance, and the volume of gas sampled was measured with a dry-type bellows meter. A calibrated orifice meter, preceding the gas meter, was used to control the instantaneous sampling rate. Corrections were applied for meter temperature, meter pressure, barometric pressure, and humidity.

Temperatures of combustion gases were measured (1) at the top of the mixing chamber just after passing the bridge wall throat and ahead of the secondary air inlets, (2) at the bottom inlet to the final combustion chamber after passing under the curtain wall, (3) at the top of the final combustion chamber just before entering the breeching, and (4) in the stack near the particulate-and gas-sampling points. In order to achieve quick response to temperature changes, the thermocouple

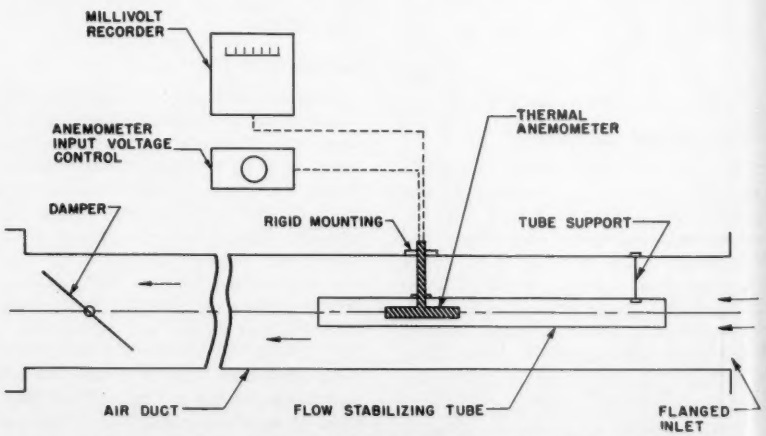

Fig. 4. Arrangement for mounting of thermal anemometer in air supply duct.

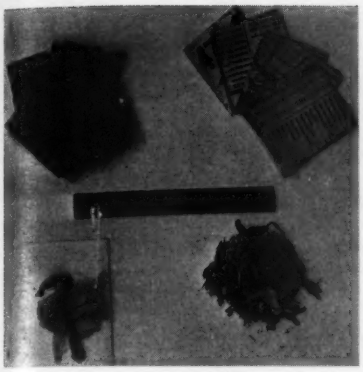

Fig. 5. Fuel components.

mass was kept small by using 30-gauge wires inside a $^1/_{16}$-inch O.D. inconel sheath. Hot junctions of the thermocouples were shielded against refractory radiation by triple concentric, cylindrical shields made of 0.012-inch inconel. Refractory temperatures were measured at three points along the arch length by hot junctions imbedded in the refractory $^1/_4$ inch from the hot surface and at two points in the final combustion chamber one inch and $1^1/_2$ inch from the hot surface.

Experiment Design

As an initial phase of the long-range study, a series of preliminary tests was necessary to provide a sound basis for the selection of certain test procedures and levels of variables which would insure accumulation of comparative data on the over-all study. Factors of particular concern with regard to firing practices were (1) amount of fuel per charge, (2) combustion rate, and (3) duration and interval of stoke. Factors of concern with regard to combustion air were (1) levels of excess combustion air, and (2) distribution of overfire, underfire, and secondary combustion air.

Fig. 6. Fuel preparation facilities.

Fig. 7. Instrument panel.

In order to evaluate the effects of these independent variables, a one-quarter fractional factorial experiment with one replication was chosen because it promised the greatest amount of information for the effort expended. Replicate tests were felt to be essential at this stage in order to provide some measure of the degree of reproducibility possible with this type of testing. The variables and the levels chosen for comparison are as follows:

Variables	Levels
Excess air	50% and 150%
Underfire air	15% and 30% of total combustion air
Secondary air	0% and 20% of total combustion air
Fuel per charge	10 lb and 15 lb
Charging rate	140 lb/hr[a] and 180 lb/hr[b]
Stoking interval	10 min and 20 min

[a] Equivalent to a grate loading of 16.5 lb/ft² hr.

[b] Equivalent to a grate loading of 21.2 lb/ft² hr.

Levels were selected to yield approximately equal effects on contaminant discharges. Thus, it was intended that the effect produced by a change in the level of one variable would not be so great that experimental errors involved in measuring the effect would obscure the effects produced by changes in levels of the remaining five variables. Limitations in these choices were those inherent in selecting levels of variables about which very little is known. For this reason, two, rather than three, levels of variables were initially selected. On the basis of results yielded by this study, third and fourth levels of variables will be selected to permit more detailed investigation of contaminant response.

The combinations of testing conditions resulting from this design are shown in Fig. 10. Two tests were made with each of the 16 combinations giving a total of 32 tests.

The grate loadings of 16.5 and 21.2 lb/ft² hr used in these tests coincide with those reported by Rose and Crabaugh[1] for units operating at comparable combustion rates. However, higher grate loadings will result from higher combustion rates obtained with increased excess combustion air levels and/or higher underfire air ratios.

Testing Procedure

The conduct of all tests followed the same procedure. The incinerator was preheated with soft coal, refuse, or natural gas to raise the refractory surface temperatures to near their operating levels. Weighed amounts of fuel were then added at predetermined intervals to maintain the desired feed rate. Combustion air was adjusted to the desired amount and distribution, and maintained at this level throughout the test. Although several hours of

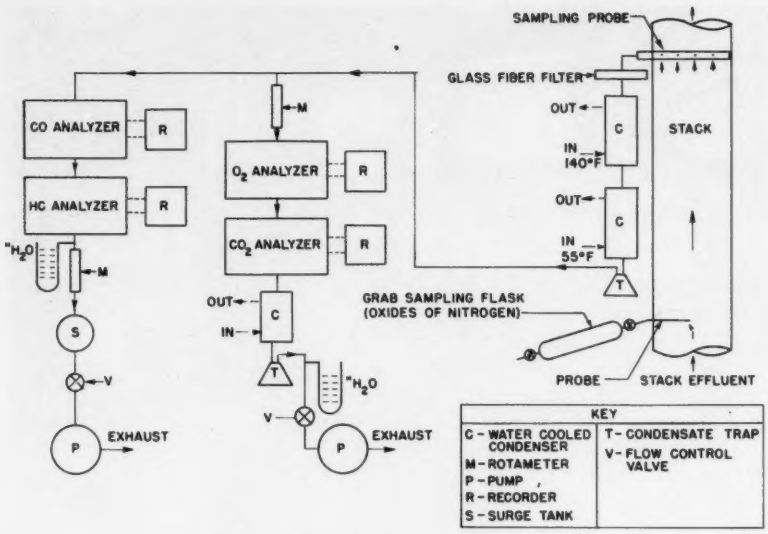

Fig. 8. Diagram of stack gas sampling system.

firing were required to achieve thermal equilibrium of the refractory an inch or more from the hot surface, refractory temperatures only 1/4 inch from the surface stabilized after 30 to 60 minutes of operation on a regular charging schedule. Uniform heat input to the refractory was assumed once this latter condition was realized. With surface refractory temperatures in the arch stabilized and gas temperatures varying uniformly over a given charging cycle, a material balance through the incinerator was made based on (1) the mass gas flow from the stack, and (2) the mass gas input to the incinerator, calculated from total combustion air and burning rate. Upon determining that the mass balance was satisfactory, all continuous gas analyzers and the particulate sampling system were started. Nitrogen oxide samples were collected over a convenient charging cycle while gas and particulate sampling was in progress. An average of nine grab samples were taken over one cycle which included the period between two charges of fuel.

Fuel Charging Technique

In this series of tests, effects of both 10-lb and 15-lb fuel charges were studied. The charging procedure involved placement of 5-lb sacks of fuel, one at a time, in the air-lock compartment (Fig. 11). Each sack was then pushed through the charging port into the incinerator and the contents spread out over the front third of the grate. Just before introducing a new charge, material from the previous charge was pushed to the rear of the grate. At scheduled intervals the fuel bed was stoked and the fuel spread over the entire grate area. Immediately after stoking, the movable grates at the back were shaken, but only enough to loosen any compacted material.

Results

Results obtained from this series of tests can be interpreted only in terms of the conditions under which the study was made. Tests were limited to a uniformly prepared rubbish of 25% moisture content which was burned under closely controlled conditions of charging and air distribution in a fixed dimension, multiple-chamber incinerator. It is not known at this time whether or not results reported here will be applicable to municipal and industrial incinerators in general. Correlation between discharges produced under these test conditions and the pollutants resulting from full-scale incinerators will be made as the study progresses, and as similar emission data are obtained from municipal incinerators operating under actual conditions.

Reproducibility of contaminant occurrence was highly dependent on good control of combustion air to the incinerator. Table I compares the nominal and actually achieved air distribution. At the 150% excess air level, where control of air flow was more difficult than at the 50% excess air level, variation in contaminant samples is correspondingly greater.

All particulate and nitrogen oxide measurements were converted to logarithms to normalize the distribution of experimental errors. The fact that the logarithms of the observations are distributed more nearly normally than the observations implies that experimental errors in measurement are proportional to the contaminant concentration measured.

A tabulation of all major findings is contained in Tables IIA and IIB. The relationship of each contaminant studied to experimental variables is discussed in turn.

1. Solid Contaminants

All conditions of combustion tested gave exceptionally low particulate emissions. In this series, the highest average particulate loading for duplicate tests was 6.1 lb per ton of fuel charged, and this occurred at the 50% excess combustion air level with 30% underfire air, 0% secondary air, and a fuel charging rate of 140 lb/hr.

Evaluation of the significance of the six variables incorporated in the experiment design indicated significant effects on particulate occurrence due to (1) percent excess combustion air, and

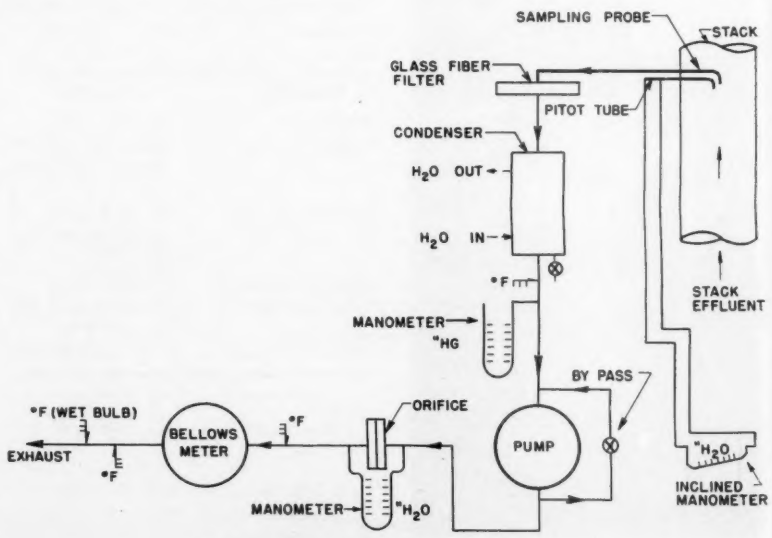

Fig. 9. Diagram of particulate sampling system.

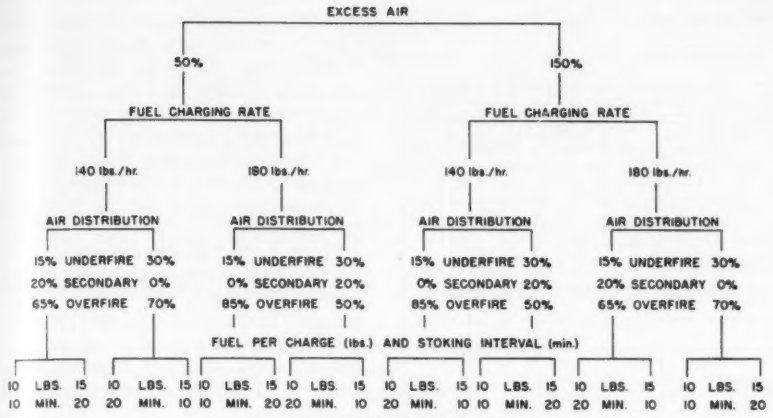

Fig. 10. Experiment design.

(2) percent underfire air. By reference to Table III it will be noted that there was little or no effect on particulates with an increase of underfire air at the 150% excess air level; but at the 50% excess air level an increase in underfire air from 15% to 30% (of the total combustion air) caused a 210% increase in particulate loadings (both in lb particulate/hr and in lb particulate/lb of fuel charged). From this it is apparent that underfire air affects particulate loadings at only one of the two excess combustion-air levels selected.

There were no significant effects on particulates attributable to (1) fuel charging rate, (2) stoking interval, (3) percent secondary air, and (4) lb of fuel per charge.

The standard deviation of experimental errors in particulate determination as computed from duplicate runs was 37.4% for measurements of either lb particulate/hour or lb particulate/lb of fuel burned.

The fact that combustion of fuel with 150% excess combustion air at 30% underfire produced significantly lower particulate loadings than 50% excess combustion air at 30% underfire, suggests the need for investigating the effects of high underfire air levels at excess combustion-air levels of 150% and above.

One of the common concepts regarding particulate discharge from municipal and industrial incineration processes is that total solid emissions result solely from physical entrainment of particules in the gas stream, with particulate discharge increasing with increased gas velocity through the fuel bed. In an effort to confirm this concept, the effects of gas velocity through the fuel bed (a function of percent underfire air) on particulate emissions were compared at the 50% and 150% excess air levels. At the 50% excess air level the solid discharge was 0.000739 lb/lb fuel at 15% underfire air, and 0.002291 lb/lb fuel at 30% underfire air. This increase in particulates with increased underfire air was not present, however, at the 150% excess air level where discharges were 0.000832 lb/lb fuel at 15% underfire air and 0.000875 lb/lb fuel at 30% underfire air. It can be concluded from these discrepancies that the concept of physical entrainment of solids as the sole mechanism for producing total solid emissions is not valid. While physical entrainment probably contributes to the discharge of particulates, other factors such as volatilization and condensation of inorganic compounds and incomplete combustion also affect the degree of this discharge.

Design of the test incinerator was based on relationships of grate loading, arch height, and length-to-width ratio of ignition chamber proposed by Rose and Crabaugh[1] as being the most suitable criteria for effecting combustion with a minimum discharge of particulates from incineration processes. The exceptionally low particulate loadings resulting from these tests tend to substantiate these design relationships for the criteria employed. Dimensions of the test incinerator are shown in Table IV.

2. Hydrocarbons

Hydrocarbons were measured and reported in terms of hexane, the sensitizing gas in the infrared analyzer. It is recognized that a hexane-sensitized instrument has zero sensitivity to acetylene and very low sensitivity to ethylene, acetone, benzene, and other organic compounds which are normally encountered in incinerator flue gases. However, this instrument is intended to serve only as an indicator of the changes in levels of organics in general, and is not intended to give a measure of total organics. The measuring system, consisting of the analyzer and millivolt recorder, has a calculated accuracy of ±17 ppm over the 30-to-750 ppm range. Experience in calibration and sampling indicate that the system cannot reliably detect hydrocarbon concentrations of less than 30 ppm.

a. Results at 50% Excess Combustion-Air Level

Combustion of fuel at this excess

TABLE 1—RANGE OF COMBUSTION AIR DISTRIBUTION

		Nominal Percentage	Range of Actual Percentages
EXCESS COMBUSTION AIR		50	42 - 49
		150	132 - 148
PERCENT OF TOTAL AIR	UNDER FIRE	15	14 - 16
		30	27 - 30
	SECONDARY	0	0
		20	19 - 22
	OVER FIRE	50	49 - 53
		65	63 - 66
		70	70 - 73
		85	84 - 86

Fig. 11. Fuel charging procedure.

TABLE 2A—SUMMARY OF RESULTS

Operation at 50% Excess Air Level

TEST CONDITIONS			TEST NO.	STACK DISCHARGE (scfm)	PARTICULATES		NITROGEN OXIDES		CARBON MONOXIDE	HYDRO-CARBONS
Fuel Burned	Air Distribution	Fuel per Charge / Stoking Interval			gr/scf	lbs/ton burned	ppm	lbs/ton burned	lbs/ton burned	lbs/ton burned
140 lbs/hr	15% Underfire and 20% Secondary	10 lbs / 10 min	11	250	0.11	1.6	80	2.1	12.	0.72
			15	240	0.044	1.3	83	2.0	0.00	0.00
		15 lbs / 20 min	4	250	0.034	0.96	66	1.6	-	-
			8	250	0.068	1.9	74	1.7	9.8	0.78
	30% Underfire and 0% Secondary	10 lbs / 20 min	20	220	0.22	5.9	69	1.6	28.	2.1
			24	270	0.13	4.1	65	1.8	18.	0.82
		15 lbs / 10 min	27	270	0.17	5.7	74	2.1	-	-
			31	250	0.21	6.4	65	1.6	26.	2.5
180 lbs/hr	15% Underfire and 0% Secondary	10 lbs / 10 min	10	330	0.049	1.6	62	1.6	4.8	0.50
			14	320	0.10	3.2	79	2.0	6.1	0.47
		15 lbs / 20 min	1	320	0.068	2.1	78	2.0	-	-
			5	300	0.057	1.6	85	2.0	4.3	0.00
	30% Underfire and 20% Secondary	10 lbs / 20 min	17	300	0.27	8.6	79	2.1	24.	1.4
			21	310	0.086	2.5	95	2.8	7.7	0.37
		15 lbs / 10 min	26	320	0.15	4.4	91	2.3	-	-
			30	330	0.072	2.3	75	2.0	8.0	0.64

air level produced measurable concentrations of hydrocarbons under all conditions of operation. However, hydrocarbon production was intermittent, each occurrence lasting only one or two minutes depending on the combination of conditions responsible for its production. When air control was precise from one charging cycle to the next, hydrocarbon surges showed a uniformly reproducible pattern over consecutive cycles (Fig. 12). Maximum concentrations ranging up to 400 ppm were produced with 50% excess air distributed between overfire and underfire. Under the conditions tested, the introduction of 20% secondary air at this excess air level did not produce any discernible change in hydrocarbon emissions.

Brief surges of hydrocarbons in the flue gases occurred when flash burning resulted from both (1) introduction of fuel to the incinerator and (2) agitation of the burning fuel bed. Although the hydrocarbon surge probably resulted from lowering of oxygen content in the fuel-bed combustion zone to levels which precluded complete combustion, the oxygen concentration measured in the stack cannot provide sufficiently precise data to establish exact values for these combustion-zone oxygen levels.

In these tests oxygen content of combustion gases averaged 10%. The lowest levels recorded were between 2% and 3% oxygen in the flue gas, but hydrocarbon peaks often occurred at considerably higher recorded oxygen concentrations. In view of the limited sensitivity of the thermal conductivity method of measuring oxygen, it is conceivable that the oxygen content may have been well below these values during brief periods of intense burning. Minimum oxygen levels occurred after charging 15 lb of fuel per charge at the 140 lb/hr burning rate.

b. Results at 150% Excess Combustion-Air Level

All conditions of combustion at 150% excess air, both with and without secondary air, failed to produce hydrocarbons in excess of the 30 ppm lower limit of detectability of the measuring system (Fig. 13). At this level of excess air there was no significant difference in the total amount of hydrocarbons produced by varying (1) the fuel charging rate, (2) the stoking interval, (3) the distribution of combustion air, or (4) the lb of fuel per charge.

Oxygen concentration averaged 14% for all tests conducted at the 150% excess air level. The lowest values recorded at this level varied between 6% and 7% oxygen in the stack gas. These values occurred after charging 15 lb of fuel/charge during the 140 lb/hr burning rate.

3. Carbon Monoxide

Accuracy of the carbon monoxide monitoring system, including the infrared analyzer and millivolt recorder was calculated to be ±0.07% CO over the 0.1% to 5% range. Calibration and extended use of the instrument showed that carbon monoxide concentrations lower than 0.1% could not be reliably detected.

Carbon monoxide content of the flue gases followed exactly the same trends as the hydrocarbons. Except for the unexplainable occurrence of carbon monoxide on a single duplicate test, all conditions of combustion at the 150% excess air level failed to produce concentrations of carbon monoxide in excess of the 0.1% lower limit of detectability (Fig. 13).

As was the case with hydrocarbons, combustion of fuel at the 50% excess air level produced intermittent surges

TABLE 2B—SUMMARY OF RESULTS

Operation at 150% Excess Air Level

TEST CONDITIONS			TEST NO.	STACK DISCHARGE (scfm)	PARTICULATES		NITROGEN OXIDES		CARBON MONOXIDE	HYDRO-CARBONS
Fuel Burned	Air Distribution	Fuel per Charge / Stoking Interval			gr/scf	lbs/ton burned	ppm	lbs/ton burned	lbs/ton burned	lbs/ton burned
140 lbs/hr	15% Underfire and 0% Secondary	10 lbs / 20 min	25	400	0.047	2.3	51	2.1	-	-
			29	390	0.042	2.0	53	2.1	0.00	0.00
		15 lbs / 10 min	18	380	0.037	1.7	68	2.4	0.00	0.00
			22	440	0.037	2.0	64	2.9	0.00	0.00
	30% Underfire and 20% Secondary	10 lbs / 10 min	2	400	0.040	2.0	48	1.9	-	-
			6	370	0.036	1.6	54	2.0	0.00	0.00
		15 lbs / 20 min	9	350	0.038	1.6	68	2.2	4.3	0.00
			13	370	0.024	1.1	52	2.0	0.00	0.00
180 lbs/hr	15% Underfire and 20% Secondary	10 lbs / 20 min	28	490	0.036	1.7	75	2.9	0.00	0.00
			32	480	0.035	1.6	60	2.2	0.00	0.00
		15 lbs / 10 min	19	510	0.029	1.4	47	1.9	0.00	0.00
			23	490	0.034	1.6	66	2.6	0.00	0.00
	30% Underfire and 0% Secondary	10 lbs / 10 min	3	500	0.058	2.8	60	2.4	-	-
			7	580	0.042	2.1	55	2.3	0.00	0.00
		15 lbs / 20 min	12	490	0.035	1.6	54	2.1	0.00	0.00
			16	450	0.036	1.6	58	2.1	0.00	0.00

TABLE 3—GEOMETRIC MEAN PARTICULATE DISCHARGE

(Means of Eight Tests)

	Lbs. particulate/hour		Lbs. particulate/lb. fuel burned	
	50% Excess Air	150% Excess Air	50% Excess Air	150% Excess Air
15% Underfire Air	1.18×10^{-1}	1.52×10^{-1}	7.39×10^{-4}	8.52×10^{-4}
30% Underfire Air	3.64×10^{-1}	1.89×10^{-1}	22.91×10^{-4}	8.75×10^{-4}

TABLE 4—INCINERATOR DIMENSIONS AND GAS VELOCITY RANGES

ZONE	DIMENSIONS		AREA OF CROSS SECTION	GAS VELOCITY RANGE*	
	ft. (Unless otherwise shown)		ft^2	ft/sec	
				50% Excess Air	150% Excess Air
Primary Combustion Chamber	Length	4.1	-	-	-
	Width	2.1			
	Maximum Arch Height Above Grate	2.7			
Flame Port	Width	2.08	0.96	14 to 24	19 to 34
	Height	0.46			
Mixing Chamber	Length	1.2	2.5	6 to 10	9 to 13
	Width	2.1			
Curtain Wall Port	Width	1.9	2.1	5 to 8	7 to 11
	Height	1.1			
Secondary Combustion Chamber	Length	2.3	4.8 (lxw)	3 to 5	4 to 6
	Width	2.1			
	Height	3.4			
Grates	Pipe O.D. (inches)	1.3	1.9	0.3 to 0.8	0.5 to 1.3
	Separation (inches)	0.4			

*Based on Average Cycle Temperature

of CO for short periods up to two minutes' duration (Fig. 12). The occurrence of measurable amounts of CO in the flue gas was directly traceable to those factors which momentarily reduce the oxygen content in the fuel-bed combustion zone below the level required for complete combustion. In some tests instantaneous CO concentrations reached $3^1/_2\%$, but these peaks were of such short duration that the highest average CO concentration for any single test amounted to only 0.2%.

As nearly as could be determined with the measuring and recording instruments used, the occurrences of carbon monoxide and hydrocarbons always coincided and were of approximately the same duration.

The findings relating to hydrocarbon and carbon monoxide concentrations can be applied to industrial and municipal incinerator design and operating practices. Since combustion at the 50% excess air level produced these contaminants while operation at the 150% excess level produced essentially no detectable concentrations, it is apparent that these contaminant discharges are a function of proper employment of combustion air as it relates to (1) distribution within the ignition chamber, and (2) levels of oxygen available in the combustion zone.

4. Oxides of Nitrogen

Up to nine individual stack-gas grab-samples per charging cycle were collected and used to determine oxides of nitrogen in the stack effluent by a technique employing the reagents recommended by Saltzman.[2] Time between samples was adjusted to assure the measurement of peaks produced by various operating conditions. Grab samples yielded instantaneous values of nitrogen oxides in the flue gas. An average value of nitrogen oxides concentration, representative of operating conditions during the sampling cycle, was obtained by integrating beneath the nitrogen-oxides time-of-sampling curve.

Preliminary studies indicated that the larger portion of nitrogen oxides in the stack effluent was in the form of nitric oxide. The reagent recommended by Saltzman is sensitive only to nitrogen dioxide. Laboratory evaluation of the reagent, using prepared samples of nitric oxide and nitrogen dioxide in air, was undertaken to determine:

1. NO to NO_2 conversion time
2. Time required for complete absorption of NO_2 by the reagent

Stack gas samples were also analyzed to determine if these laboratory findings can be applied to the measurement of nitrogen oxides in a complex stack-gas mixture. The curves in Fig. 14 show the nitrogen dioxide concentrations of three replicate sets of flue-gas samples, measured with the Saltzman reagent, after various sample holding times up to forty-eight hours. On the basis of these results and the findings made

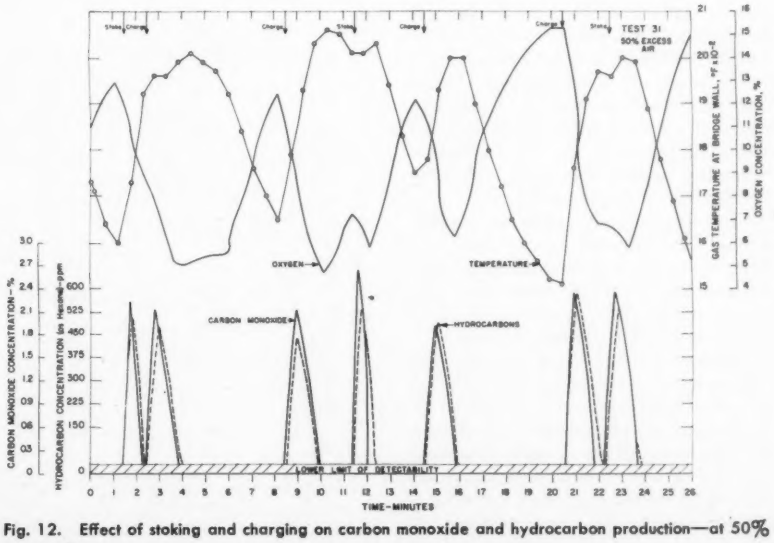

Fig. 12. Effect of stoking and charging on carbon monoxide and hydrocarbon production—at 50% excess air.

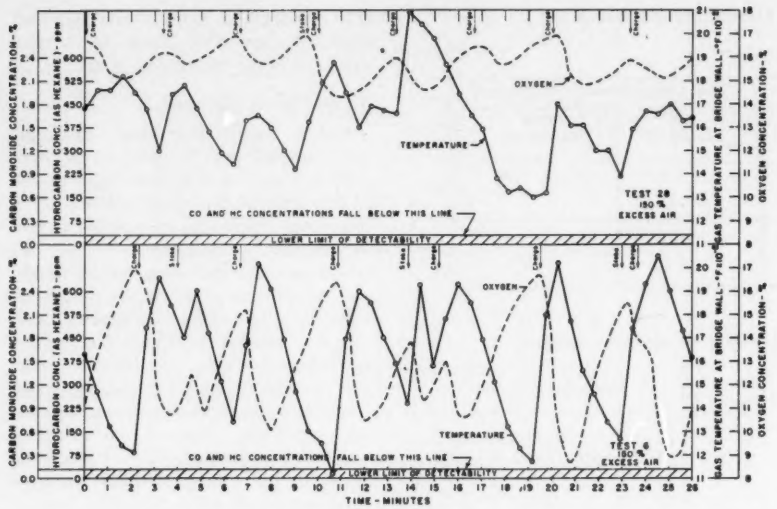

Fig. 13. Effect of stoking and charging on carbon monoxide and hydrocarbon production—at 150% excess air.

using prepared gas samples in the laboratory, all subsequent determinations of nitrogen oxides were based on spectrophotometric evaluation of Saltzman reagent absorbance, after twenty-four hours had been allotted for complete conversion of NO to NO_2, absorption of the NO_2, and full color development of the absorbing reagent. All oxides of nitrogen are therefore reported as NO_2. A detailed discussion of this work will be published separately.

Variables found to be significant in the formation of nitrogen oxides were excess air and feed rate. No distinguishable effects on NO_2 were produced by (1) lb of fuel per charge, (2) stoking interval, (3) percent secondary air, and (4) percent underfire air. The main effect attributable to excess combustion air was a 12% increase in lb NO_2/hr (0.156 lb/hr to 0.174 lb/hr) and a 12% increase in lb NO_2/lb fuel burned (0.000982 lb NO_2/lb fuel to 0.0001096 lb NO_2/lb fuel), Table V.

The main effect attributable to feed rate was a 44% increase in lb NO_2/hr (0.137 lb NO_2/hr to 0.198 lb NO_2/hr) and a 12% increase in lb NO_2/lb fuel burned (0.000980 lb NO_2/lb fuel burned to 0.001098 lb NO_2/lb fuel burned).

The standard deviation of experimental errors computed from differences between nitrogen oxides discharges from duplicate runs was found to be 12.4% for measurements of lb NO_2/hr and lb NO_2/lb fuel burned.

Temperature fluctuations of the combustion gases at the bridge wall followed a cyclic pattern which involved a rapid increase of temperature shortly after fuel was charged, and a gradual decrease of temperature as combustion continued. Under all test conditions, high instantaneous concentrations of nitrogen oxides in the flue gas occurred when gas temperatures at the bridge wall were high. As gas temperature at the bridge wall decreased, concentrations of nitrogen oxides generally decreased. This behavior pattern is illustrated by Fig. 15. In some instances, concentrations peaked while gas temperature showed no extreme change. This behavior can be explained by the fact that gas temperature at the bridge wall is measured at 32-second intervals and sudden temperature fluctuations between measurements escape detection. Also, small localized regions of rapid burning in the fuel bed apparently have a greater relative effect on nitrogen oxides concentrations in the stack than on gas temperature at the bridge wall.

In addition to fuel charging, agitation of the burning fuel bed was also responsible for increased burning as revealed by high gas temperatures at the bridge wall and correspondingly high nitrogen oxides concentrations.

The critical temperature associated with the formation of nitrogen oxides is thought to be in or directly over the fuel bed, but gas temperature at the bridge wall may be a usable indicator of nitrogen oxides concentration in the effluent. Before establishing the relationship between the two, the reproducibility of burning conditions as reflected by these parameters must be firmly established.

Comparison of nitrogen-oxides gas-temperature patterns for two complete non-consecutive charging cycles within the same test shows consistency (Fig. 16). Similarly, comparison of this relationship for two complete cycles of duplicate tests employing identical operating conditions shows this same consistency (Fig. 17). Consistency is exhibited for similar patterns of all tests, but the degree of reproducibility varies. When duplication of combustion conditions for duplicate runs is good, the resulting patterns are also good. Thus, at the 150% excess air level, where combustion air flow is more difficult to control than at the 50% excess air level, nitrogen-oxides gas-temperature patterns indicate greater variation (Fig. 18).

Despite changes in levels of all variables considered in this study, nitrogen oxides concentrations in the effluent is highly associated with gas temperature at the bridge wall. For this reason it is felt that gas temperature at the bridge wall is a usable indicator of the order of magnitude of nitrogen oxides concentration in the effluent. It is possible that experimental variables found in this study to be significantly related to oxides of nitrogen emission are effective only through their influence on temperature. Deviations from the

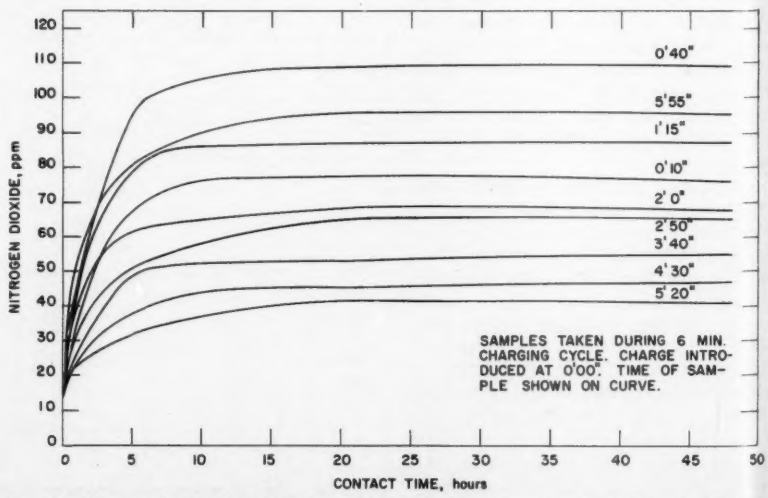

Fig. 14. Nitrogen dioxide in stack effluent grab samples based on analysis with Saltzman Reagent.

TABLE 5—GEOMETRIC MEAN OF NITROGEN OXIDES DISCHARGE

	Lbs. NO_2/hour			Lbs. NO_2/lb. fuel burned		
	50% Excess Air	150% Excess Air	Average	50% Excess Air	150% Excess Air	Average
140 lbs. fuel/hr.	1.26×10^{-1}	1.49×10^{-1}	1.37×10^{-1}	9.02×10^{-4}	10.65×10^{-4}	9.80×10^{-4}
180 lbs. fuel/hr.	1.98×10^{-1}	2.03×10^{-1}	1.98×10^{-1}	10.70×10^{-4}	11.28×10^{-4}	10.98×10^{-4}
Average	1.56×10^{-1}	1.74×10^{-1}		9.82×10^{-4}	10.96×10^{-4}	

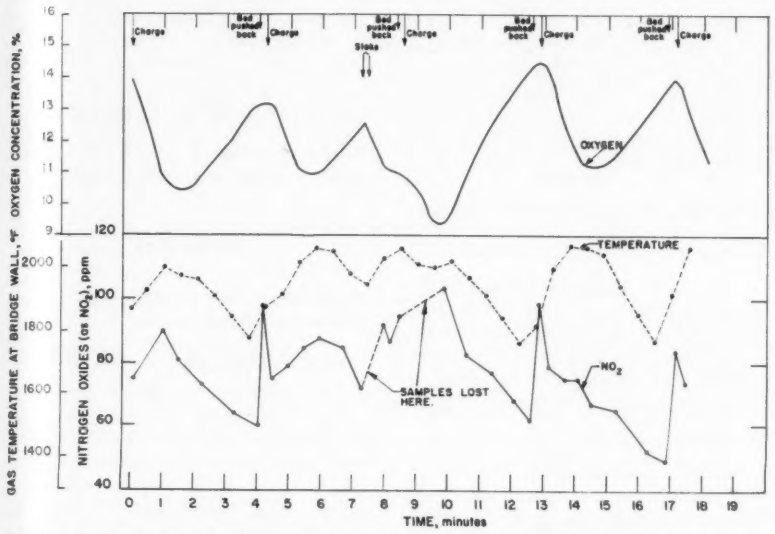

Fig. 15. Cyclic variation of oxides of nitrogen and temperature showing effect of stoking and charging.

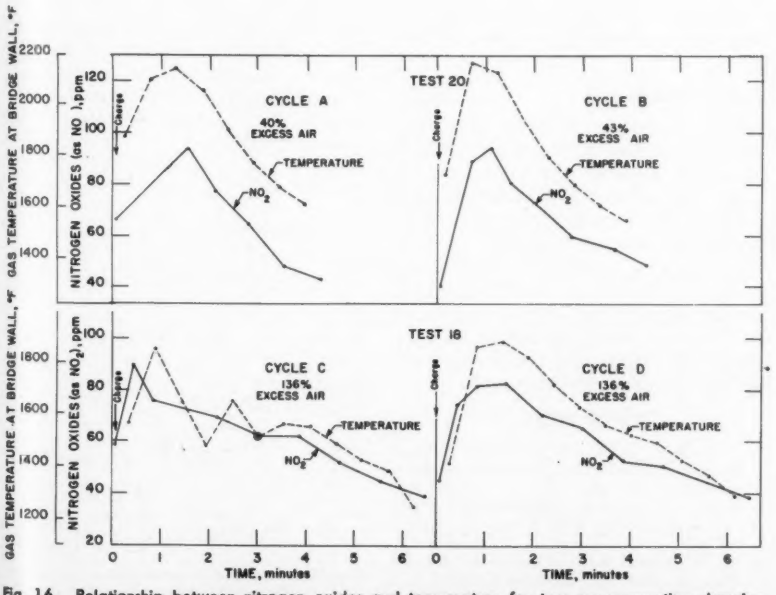

Fig. 16. Relationship between nitrogen oxides and temperature for two non-consecutive charging cycles.

desired excess air level caused more or less dilution of the nitrogen oxides, and all concentrations used to evaluate the relationship between nitrogen oxides and gas temperature were corrected to provide a comparative basis for evaluation. The correction applied was:

$$NO_2, \text{ ppm at nominal air level} = NO_2 \text{ (ppm)} \times \frac{\text{(Combustion air, actual)}}{\text{(Combustion air, nominal)}}$$

Figs. 19 and 20 show curves obtained from linear regression analyses performed on values of nitrogen oxides concentrations and the corresponding gas temperature at the bridge wall for all samples collected at the 50% and 150% excess combustion air levels, respectively. The method of least squares was used. The resulting straight lines have the following equations:

50% Excess Combustion Air:

$$\text{Log } NO_2 \text{ (ppm)} = 0.0003689T \text{ (°F)} + 1.1625 \pm 0.1253$$

150% Excess Combustion Air:

$$\text{Log } NO_2 \text{ (ppm)} = 0.0004056T \text{ (°F)} + 1.0784 \pm 0.1970$$

There is no major difference between the slopes or intercepts of these curves; however, dispersion of sample points at the 150% excess combustion air level is greater than at the 50% excess air level.

The most significant findings of this study which can be applied to municipal and industrial incineration are the three factors affecting the formation of oxides of nitrogen: (1) temperature, (2) excess air, and (3) feed rate (grate loading).

The concentration of nitrogen oxides did not increase linearly with temperature, but did increase as a logarithmic function of temperature. While gas-temperature at the bridge wall was the indicator in this relationship, it is realized that ignition-zone temperatures are controlling. Of import to incinerator design, however, is the fact that increased operating temperatures result in increased formation of nitrogen oxides, other conditions being equal.

Increasing the excess combustion air resulted in increased formation of nitrogen oxides for a given grate loading, despite the accompanying reduction in temperature. The effect of decrease in temperature with its corresponding decrease in oxides of nitrogen is apparently a less significant shift than the increase in oxides of nitrogen due to higher excess combustion air. This

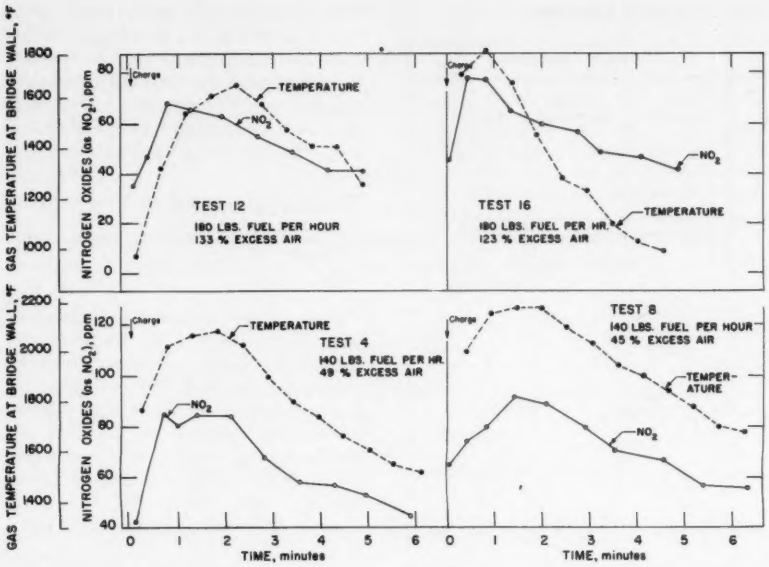

Fig. 17. Relationship between nitrogen oxides and temperature for charging cycles of replicate tests.

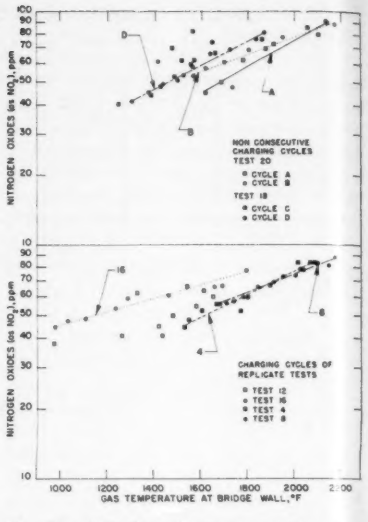

Fig. 18. Variation of nitrogen oxides—temperature relationship between test cycles.

relationship should hold for larger incinerators where the temperature decrease will be less for a corresponding increase in excess air, since the surface-to-volume ratio, for heat loss, will also be smaller. From an operational standpoint, this effect is significant in that practices of reducing furnace temperatures through the use of high levels of excess air may result in increased total discharge of oxides of nitrogen.

As in the case of excess air, an increase in feed rate resulted in an increase in the formation of oxides of nitrogen. The cause, however, is obscured since the ignition-chamber temperature also increased with increased feed rate at a given excess air level and the effect may be a result of temperature increase. This effect, from the operational and design standpoint, is significant in that increased grate loadings can be expected to result in increased emissions of nitrogen oxides.

5. Smoke and Odors

While it is realized that smoke and odor levels from incineration processes do not constitute accurate measurements of contaminant discharges, sufficient observations of both smoke and odors were made during these tests to establish gross levels. Random observations indicated smoke density to be essentially zero, and the odor level was sufficiently low to be undetectable in the immediate vicinity of the stack.

Acknowledgment

Acknowledgment is made to A. P. Altshuller and to A. Wartburg, of the Chemical Research and Development Unit, for advice and direction on many of the chemical aspects of the study, and for participation in the NO_2 sampling studies, respectively; and to E. Harris and K. Busch, Analytical Statisticians of the Sanitary Engineering Center, for setting up the experiment design and performing the statistical evaluation of the results.

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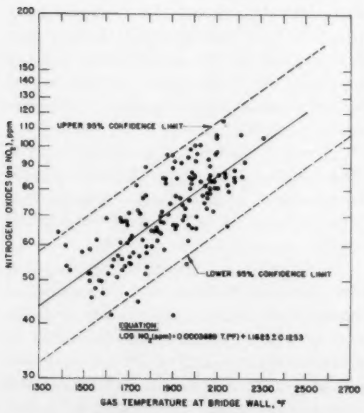
NITROGEN OXIDES (as NO2), ppm
UPPER 95% CONFIDENCE LIMIT
LOWER 95% CONFIDENCE LIMIT
EQUATION
GAS TEMPERATURE AT BRIDGE WALL, °F

Fig. 19. Relationship of nitrogen oxides to temperature at 50% excess combustion air level (all samples).

APPENDIX

Experiment Design and Method of Analysis

A. BUSCH and K. HARRIS

The experimental design employed was a $1/4$-replicate fractional factorial replicated twice. Thirty-two runs were performed, consisting of duplicate runs under each of 16 sets of controlled experimental conditions. These 16 sets are $1/4$ of a two^6 factorial experiment testing two levels of each of six variables.

Of course, testing only one-fourth of the $2 \times 2^6 = 128$ trials which would be required for a complete factorial experiment replicated twice involves some loss of information, but through careful choice of test conditions, this loss can often be restricted to comparisons which either are of no interest or

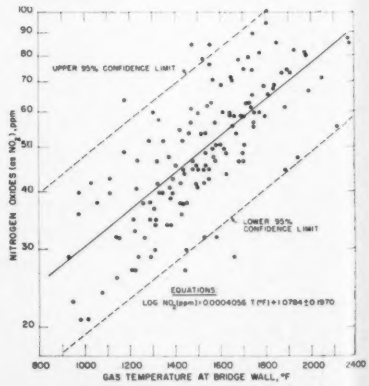
NITROGEN OXIDES (as NO2), ppm
UPPER 95% CONFIDENCE LIMIT
LOWER 95% CONFIDENCE LIMIT
EQUATIONS
GAS TEMPERATURE AT BRIDGE WALL, °F

Fig. 20. Relationship of nitrogen oxides to temperature at 150% excess combustion air level (all samples).

are known to be of little or no significance. The experimental design "confounds" the main effects and interaction-effects of the six variables into 15 sets of four confounded effects per set. By "confounded effects," we mean a group of effects whose joint or "total" effect is measurable, but in which this total effect cannot be distributed quantitatively among the members of the group.

For each of these 15 sets, a contrast was made between two means of the logarithms of 16 observations per mean, and 95% confidence limits for the difference between these two means of logs were computed and converted to 95% confidence limits for the ratio between the two true geometric means (in the original units of measurement). The measurements were converted to logarithms to normalize the distribution of experimental errors. The fact that the logs of the observations are more nearly normally distributed than the observations themselves implies that experimental errors of measurement are proportional to the amounts measured. The experimental error between duplicate runs was used to determine the widths of confidence intervals.

As an example of the interpretation of significant contrasts, consider that the geometric mean NO_2 emission at the 140 lb/hr feed rate was significantly less than the geometric mean NO_2 emission at the 180 lb/hr feed rate. This same contrast measures three other confounded effects—two three-factor interactions and one five-factor interaction—so that the difference between the two means could be caused by any one (or more than one) of these four confounded effects. But it is likely that the mean difference is attributable to the main effect (over-all average difference) of changing the feed rate, since interactions between three or more variables are usually either non-existent or are very small.

Results

In Tables I through IV, the effects which are likely to be the cause of any significant mean differences are listed in the "Effect" column, and the confounded effects which are considered unlikely to be of appreciable size are listed under "Confounded Effects." When a contrast which does not measure a main effect was found to be non-significant, all four confounded interaction-effects were listed in parallel.

Oxides of Nitrogen

Two main effects—those of excess air and feed rate—were found to be significant and there were no significant interactions. Increasing the excess air from 50% to 150% resulted in a 12% increase in lb NO_2/hr and a 12% increase in lb NO_2/lb fuel charged.

Increasing the feed rate from 140 lb/hr to 180 lb/hr caused a 44% increase in lb NO_2/hr and a 12% increase in lb NO_2/lb fuel charged.

Although there are indications that other small effects may exist, their magnitudes are too small to be distinguishable from the experimental error.

The standard deviation of experimental errors computed from differences between results from duplicate runs was found to be 0.051 log unit (about 12.4%) for measurements of lb NO_2/hr or of lb NO_2/lb fuel charged.

For five runs, values of lb NO_2/hr were obtained from two different charge-stoke cycles after the system had reached a steady state. For these five runs the variation in lb NO_2/hr between cycles, within a given run, was actually greater (but not significantly so) than the variation between (lb NO_2/hr)-values obtained from duplicate runs. In other words, it was possible to reproduce NO_2 results from run-to-run within limits as narrow as the variation from cycle-to-cycle within a given run.

Particulates

There were three significant effects involving two of the factors—two main effects, of percent underfire air and of percent excess air, and their interaction. This interaction between excess

Table I—Analysis of Variance of the Variable, $\log_{10}$ [(lb. NO_2/hr.) x 10^{-1}]

Effect	Confounded Effects	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio(1)	Geometric Mean(2) of (lb. NO_2/hr.) x 10^{-1}		Ratio of Means: $m_{(+)}/m_{(-)}$	95% Confidence Limits for Ratio of True Means(3)	
						$m_{(+)}$	$m_{(-)}$		Lower Limit	Upper Limit
A = %-Underfire Air	BxCxD BxExF AxCxDxExF	.004512	1	.004512	1.76	1.60	1.69	.95	.87	1.03
B = %-Excess Air	AxCxD AxExF BxCxDxExF	.017955	1	.017955	6.99*	1.74	1.56	1.12	1.02	1.22
C = Frequency of Charge	AxBxD DxExF AxBxCxExF	.003160	1	.003160	1.23	1.61	1.68	.96	.88	1.04
D = Frequency of Stoke	AxBxC CxExF AxBxDxExF	.004608	1	.004608	1.79	1.60	1.69	.95	.87	1.03
E = Feed Rate	AxBxF CxDxF AxBxCxDxE	.202566	1	.202566	78.85**	1.98	1.37	1.44	1.32	1.57
F = %-Secondary Air	AxBxE CxDxE AxBxCxDxF	.000032	1	.000032	.01	1.65	1.64	1.00	.92	1.10
AxB, CxD, ExF, AxBxCxDxExF		.000128	1	.000128	.05					
AxC, BxD, AxDxExF, BxCxExF		.005101	1	.005101	1.99					
AxD, BxC, AxCxExF, BxDxExF		.000253	1	.000253	.10					
AxE, BxF, AxCxDxF, BxCxDxE		.000450	1	.000450	.18					
AxF, BxE, AxCxDxE, BxCxDxF		.004851	1	.004851	1.89					
CxE, DxF, AxBxDxE, AxBxCxF		.007021	1	.007021	2.73					
CxF, DxE, AxBxCxE, AxBxDxF		.000882	1	.000882	.34					
AxCxE, AxDxF, BxCxF, BxDxE		.000000	1	.000000	.00					
AxCxF, AxDxE, BxCxE, BxDxF		.002415	1	.002415	.94					
Between Duplicate Runs (Experimental Error)		.041109	16	.002569	--					
Total		.295043	31							

(1) F-Ratio = (Mean Square for Tabulated Effect) / (Mean Square Between Duplicate Runs)
* = significantly greater than 1.00 at the 5% probability level
** = significantly greater than 1.00 at the 1% probability level

(2) $m_{(+)}$ = geometric mean NO_2 emission (lb. NO_2/hr.) for 16 runs performed at the higher level of the variable listed in the "Effect" column.
$m_{(-)}$ = geometric mean NO_2 emission (lb. NO_2/hr.) for 16 runs performed at the lower level of the variable listed in the "Effect" column.

(3) The ratio of means which would be obtained from an infinite number of runs.

Table 2—Analysis of Variance of the Variable, $\log_{10}$ [(lbs. NO_2/lb. fuel charged) x 10^{-4}]

Effect	Confounded Effects	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio(1)	Geometric Mean(2) of (lb. NO_2/lb. fuel) x 10^{-4}		Ratio of Means: $m_{(+)}/m_{(-)}$	95% Confidence Limits for Ratio of True Means(3)	
						$m_{(+)}$	$m_{(-)}$		Lower Limit	Upper Limit
A = %-Underfire Air	BxCxD BxExF AxCxDxExF	.004632	1	.004632	1.80	10.09	10.67	.95	.87	1.03
B = %-Excess Air	AxCxD AxExF BxCxDxExF	.018098	1	.018098	7.04*	10.96	9.82	1.12	1.02	1.22
C = Frequency of Charge	AxBxD DxExF AxBxCxExF	.002984	1	.002984	1.16	10.15	10.61	.96	.88	1.04
D = Frequency of Stoke	AxBxC CxExF AxBxDxExF	.004778	1	.004778	1.86	10.09	10.67	.95	.87	1.03
E = Feed Rate	AxBxF CxDxF AxBxCxDxE	.019652	1	.019652	7.64*	10.98	9.80	1.12	1.03	1.22
F = %-Secondary Air	AxBxE CxDxE AxBxCxDxF	.000014	1	.000014	.00	10.39	10.36	1.00	.92	1.10
AxB, CxD, ExF, AxBxCxDxExF		.000124	1	.000124	0.05					
AxC, BxD, AxDxExF, BxCxExF		.004975	1	.004975	1.93					
AxD, BxC, AxCxExF, BxDxExF		.000270	1	.000270	.10					
AxE, BxF, AxCxDxF, BxCxDxE		.000553	1	.000553	.22					
AxF, BxE, AxCxDxE, BxCxDxF		.004827	1	.004827	1.88					
CxE, DxF, AxBxDxE, AxBxCxF		.006933	1	.006933	2.70					
CxF, DxE, AxBxCxE, AxBxDxF		.000872	1	.000872	.34					
AxCxE, AxDxF, BxCxF, BxDxE		.000000	1	.000000	.00					
AxCxF, AxDxE, BxCxE, BxDxF		.002468	1	.002468	.96					
Between Duplicate Runs (Experimental Error)		.041159	16	.002572	--					
Total		.112339	31							

(1) F-Ratio = (Mean Square for Tabulated Effect) / (Mean Square Between Duplicate Runs)

* = significantly greater than 1.00 at the 5% probability level

(2) $m_{(+)}$ = geometric mean NO_2 emission for 16 runs performed at the higher level of the variable listed in the "Effect" column.

$m_{(-)}$ = geometric mean NO_2 emission for 16 runs performed at the lower level of the variable listed in the "Effect" column.

(3) The ratio of means which would be obtained from an infinite number of runs.

air and underfire air is confounded with two other two-factor interactions—those between frequency of charge and stoking rate and between feed rate and percent-secondary air. But because there were no significant main effects of the last-named four factors, the existence of interactions between them would mean that the effect of any one of these factors at the higher level of its interacting factor was equal in magnitude but opposite in direction to its effect at the lower level of the interacting factor. This seems an unlikely possibility, so that the significance of the contrast was attributed to an interaction between percent underfire air and percent excess air.

Table 3—Analysis of Variance of the Variable, $\log_{10}$ [(lb. Particulates/hr.) x 10^{-1}]

Effect	Confounded Effects	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio(1)	Geometric Mean(2) of (lb. Part.'s/hr.) x 10^{-1}		Ratio of Means: $m_{(+)}/m_{(-)}$	95% Confidence Limits for Ratio of True Means	
						$m_{(+)}$	$m_{(-)}$		Lower Limit	Upper Limit
A = %-Underfire Air	BxCxD BxExF AxCxDxExF	.526851	1	.526851	27.85**	2.25	1.25	1.80	1.42	2.29
B = %-Excess Air	AxCxD AxExF BxCxDxExF	.270480	1	.270480	14.30**	1.36	2.07	.66	.52	.83
C = Frequency of Charge	AxBxD DxExF AxBxCxExF	.034453	1	.034453	1.82	1.55	1.80	.86	.68	1.09
D = Frequency of Stoke	AxBxC CxExF AxBxDxExF	.001378	1	.001378	.07	1.70	1.65	1.03	.81	1.31
E = Feed Rate	AxBxF CxDxF AxBxCxDxE	.075855	1	.075855	4.01	1.87	1.50	1.25	.99	1.59
F = %-Secondary Air	AxBxE CxDxE AxBxCxDxF	.059340	1	.059340	3.14	1.52	1.85	.82	.65	1.04
A x B	CxD ExF AxBxCxDxF	.439453	1	.439453	23.23**					
AxC, BxD, AxDxExF, BxCxExF		.008911	1	.008911	.47					
AxD, BxC, AxCxExF, BxDxExF		.039621	1	.039621	2.09					
AxE, BxF, AxCxDxF, BxCxDxE		.001830	1	.001830	.10					
AxF, BxE, AxCxDxE, BxCxDxF		.011476	1	.011476	.61					
CxE, DxF, AxBxDxE, AxBxCxF		.000021	1	.000021	.00					
CxF, DxE, AxBxCxE, AxBxDxF		.006670	1	.006670	.35					
AxCxE, AxDxF, BxCxF, BxDxE		.044850	1	.044850	2.37					
AxCxF, AxDxE, BxCxE, BxDxF		.004851	1	.004851	.26					
Between Duplicate Runs (Experimental Error)		.302659	16	.018916	--					
Total		1.828699	31							

(1) F-Ratio = (Mean Square for Tabulated Effects) / (Mean Square Between Duplicate Runs)

** = significantly greater than 1.00 at the 1% probability level

(2) $m_{(+)}$ = geometric mean particulates emission for 16 runs performed at the higher level of the variable listed in the "Effect" column.

$m_{(-)}$ = geometric mean particulates emission for 16 runs performed at the lower level of the variable listed in the "Effect" column.

(3) The ratio of means which would be obtained from an infinite number of runs.

Table 4—Analysis of Variance of the Variable, $\log_{10}$ [(lbs. Particulates/lb. Fuel Charged) x 10^{-4}]

Effect	Confounded Effects	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio(1)	Geometric Mean(2) of (lb. Part.'s/lb. Fuel) x 10^{-4}		Ratio of Means:	95% Confidence Limits for Ratio of True Means(3)	
						$m_{(+)}$	$m_{(-)}$	$m_{(+)}/m_{(-)}$	Lower Limit	Upper Limit
A = % Underfire Air	BxCxD BxExF AxCxDxExF	.527365	1	.527365	27.73**	14.16	7.84	1.81	1.42	2.29
B = % Excess Air	AxCxD AxExF BxCxDxExF	.269378	1	.269378	14.16**	8.53	13.02	.66	.52	.83
C = Frequency of Charge	AxBxD DxExF AxBxCxExF	.034191	1	.034191	1.80	9.78	11.36	.86	.68	1.09
D = Frequency of Stoke	AxBxC CxExF AxBxDxExF	.001378	1	.001378	0.07	10.70	10.38	1.03	.81	1.31
E = Feed Rate	AxBxF CxDxF AxBxCxDxE	.001013	1	.001013	0.05	10.40	10.68	.97	.77	1.24
F = % Secondary Air	AxBxE CxDxE AxBxCxDxF	.059858	1	.059858	3.15	9.54	11.64	.82	.65	1.04
A x B	CxD ExF AxBxCxDxF	.439922	1	.439922	23.13**					
AxC, BxD, AxDxExF, BxCxExF		.008778	1	.008778	0.46					
AxD, BxC, AxCxExF, BxDxExF		.039621	1	.039621	2.08					
AxE, BxF, AxCxDxF, BxCxDxE		.001922	1	.001922	0.10					
AxF, BxE, AxCxDxE, BxCxDxF		.011250	1	.011250	0.59					
CxE, DxF, AxBxDxE, AxBxCxF		.000021	1	.000021	0.00					
CxF, DxE, AxBxCxE, AxBxDxF		.006670	1	.006670	0.35					
AxCxE, AxDxF, BxCxF, BxDxE		.045150	1	.045150	2.37					
AxCxF, AxDxE, BxCxE, BxDxF		.004950	1	.004950	0.26					
Between Duplicate Runs (Experimental Error)		.304315	16	.019020	--					
Total		1.755782	31							

(1) $F\text{-Ratio} = \frac{\text{(Mean Square for Tabulted Effect)}}{\text{(Mean Square Between Duplicate Runs)}}$

** = significantly greater than 1.00 at the 1% probability level

(2) $m_{(+)}$ = geometric mean particulates emission for 16 runs performed at the higher level of the variable listed in the "Effect" column.

$m_{(-)}$ = geometric mean particulates emission for 16 runs performed at the lower level of the variable listed in the "Effect" column.

(3) The ratio of means which would be obtained from an infinite number of runs.

The nature of the interaction between underfire air and excess air is shown in Table V, a table of means of eight runs each. Note that there is little or no effect of an increase in underfire air on particulates when there is 150% excess air; but that when there is only 50% excess air, increasing the underfire air from 15% to 30% causes a 210% (3.1-fold) increase in both lb particulates/hr and lb particulates/lb fuel charged.

The standard deviation of experimental errors computed from duplicate runs was 0.138 log-unit (about 37.4%) for measurements either of lb particulates/hr or of lb particulates/lb fuel charged.

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Eye IRRITATION from Irradiated AUTOMOBILE EXHAUST (Effect of Irradiation Intensity; Half-Life Studies)*

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Two major classes of pollutants found in the Los Angeles atmosphere are organic matter, particularly hydrocarbons, and oxides of nitrogen. When appropriate mixtures of these chemicals are irradiated, they interact to produce oxidants such as ozone[1] and other smog manifestations.[2-4] Automobile exhaust, as a major source of hydrocarbons and oxides of nitrogen in the Los Angeles area, has been the subject of various studies.

In 1956, an investigation was made of certain aspects of the eye-irritating capacity of irradiated mixtures containing purified air and 1000 to 2900 ppm of automobile exhaust formed during acceleration, cruising, deceleration, and idling.[5] When mixtures of certain of the exhausts were irradiated, appreciable eye irritation was reported by the experimental human subjects; no irritation was reported in the absence of irradiation. Irradiation also caused the formation of an oxidant as measured with potassium iodide[6] and nitrogen dioxide as measured with a modified Griess reagent.[7]

The investigation reported here was a further inquiry into the effects of automobile exhaust in which two series of experiments on eye irritation were carried out. The first series was designed to measure the effects of varied irradiation intensities on eye irritation and on the extent of the photochemical reaction of the oxidant and nitrogen dioxide content of an exhaust-air mixture. The second series was designed to determine the half life of the eye irritant, as indicated by the averaged, weighted reports of eye irritation in human experimental subjects. A corollary investigation determined the decay rates of certain components of the irradiated exhaust-air mixture. In this series, the half-life and decay rates were measured both with and without additional irradiation and with and without circulation of the exhaust-air mixture.

Experimental Equipment, Subjects, and Procedure

Fig. 1 is a diagram showing the flow of exhaust and air through the laboratory equipment. Automobile exhaust was obtained from an automobile mounted on a chassis dynamometer, illustrated in Fig. 2. The automobile equipped with a metal cam which operated the accelerator pedal to simulate driving is shown in Fig. 3. The drive shaft of the metal cam, which was driven by a 1-rpm electric motor, also contained plastic cams that actuated solenoid valves for sampling the exhaust. Fig. 4 shows the sampling system constructed of four variable orifice valves and solenoid valves, which controlled the rate and amount of exhaust sampling. By appropriate adjustment of the cams, valves, and orifices, any desired concentration or combination of exhausts could be obtained, whether accelerating, cruising, decelerating, or idling.

The purified air used to dilute the exhaust was outside air that had been passed over platinized alumina at 1000°F, cooled, and filtered through an activated charcoal bed. The measured amounts of exhaust-air were mixed and carried to an irradiating chamber. Irradiation was provided by twenty-four 400-watt H1 mercury arc lamps mounted outside Pyrex windows in the chamber walls. Within the chamber were a 24-inch circulating fan and temperature control equipment. The temperature of the mixture within the chamber was maintained at 26 ± 3°C by a cooling system consisting of 250 square feet of finned, stainless steel tubing through which tap water was circulated. The chamber humidity was not controlled and varied between 30 and 50 percent relative humidity.

Measurements of the effect of irradiation on chamber gases were made with the following instruments: for hydrocarbons, an infrared spectrometer; for oxidant, a potassium iodide colorimeter; for nitrogen dioxide, a recording Griess reagent colorimeter; for carbon monoxide, a non-dispersive infrared analyzer;

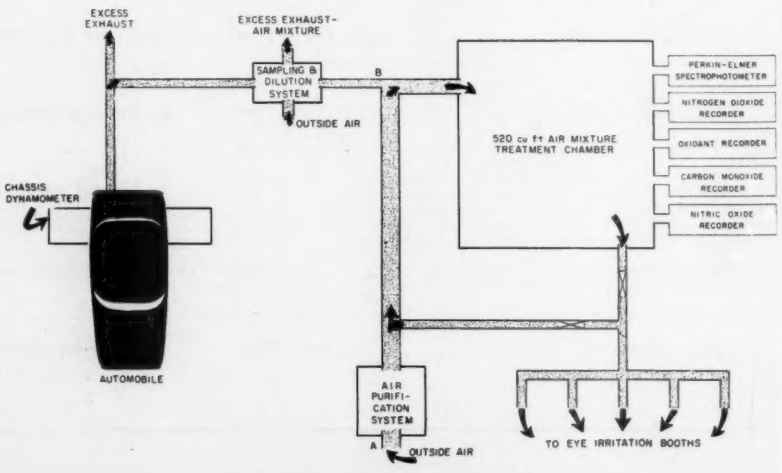

Fig. 1. Diagram of laboratory facility.

* Presented at the 132nd ACS meeting in New York, September 9, 1957.

Fig. 2. View of automobile mounted on dynamometer.

and for eye irritation, a panel of 10 human subjects. Each subject reported eye irritation as none, light, medium, or severe; these reports were assigned the values 0, 1, 2, and 3. The average of their reported observations for a particular test is used as a measure of the eye irritation and is called the eye irritation index; e.g., when all subjects report severe irritation, this index has a maximum value of 24.

Fig. 5 shows the irradiation chamber and some of the instruments used for analyzing the chamber gases. Fig. 6 shows a subject in an eye irritation booth wearing eye mask and respirator.

Results and Discussion

Irradiation Intensity Experiments

Eight experiments were conducted to determine the effect of the intensity of irradiation on eye irritation. Other substances measured were oxidant, hydrocarbons, nitrogen dioxide, and carbon monoxide. For each experiment, the exhaust-air mixture contained 2550 ppm of exhaust with the following composition: 520 ppm accelerating exhaust, 1300 ppm cruising exhaust, 660 ppm decelerating, and 70 ppm idling exhaust. For each experiment in the series, the exhaust-air mixture flowed through the chamber at the rate of 8.7 cubic feet per minute. Average residence time in the chamber was 60 minutes at about 26°C. The intensity of irradiation was varied; one experiment was carried out in the dark, two experiments had six arcs, two had 12 arcs, and three had 24 arcs. When the irradiated mixture had reached a steady state (approximately two hours), the amount of eye irritation was determined. The other components were determined with the instruments previously mentioned.

Table I summarizes the results of the first series of eight experiments. The eye irritation index as a function of the number of arcs used is presented graphically in Fig. 7. Table I shows that both oxidant and eye irritation were markedly higher with 12 or more arcs than with zero and six arcs. Carbon monoxide and hydrocarbon values remained essentially constant during this series; nitrogen dioxide values were small without irradiation, increased sharply with six-arc and 12-arc irradiation, and decreased slightly with 24-arc irradiation. An example of the concentration curves of the oxidant and nitrogen dioxide formed under 24-arc irradiation appears in Fig. 8.

Since both eye irritation and oxidant increased with the increased intensity of irradiation, it appears that under these conditions eye irritation and oxidant formation are functions of the irradiation intensity. That both were still increasing at the maximum irradiation intensity suggests that both would continue to increase with further increases in irradiation intensity. Moreover, it would appear that additional irradiation would lead to further decrease in the nitrogen dioxide values.

Half-Life Experiments

Fifteen seconds were required for the irradiated mixtures to pass from the chamber to the subjects' eye masks. If the half life of the eye irritant were only 15 seconds, the degree of eye irritation would be reduced one half in the passage of the gas from the chamber to the masks. To determine whether the eye irritation was affected by this delay, a series of experiments

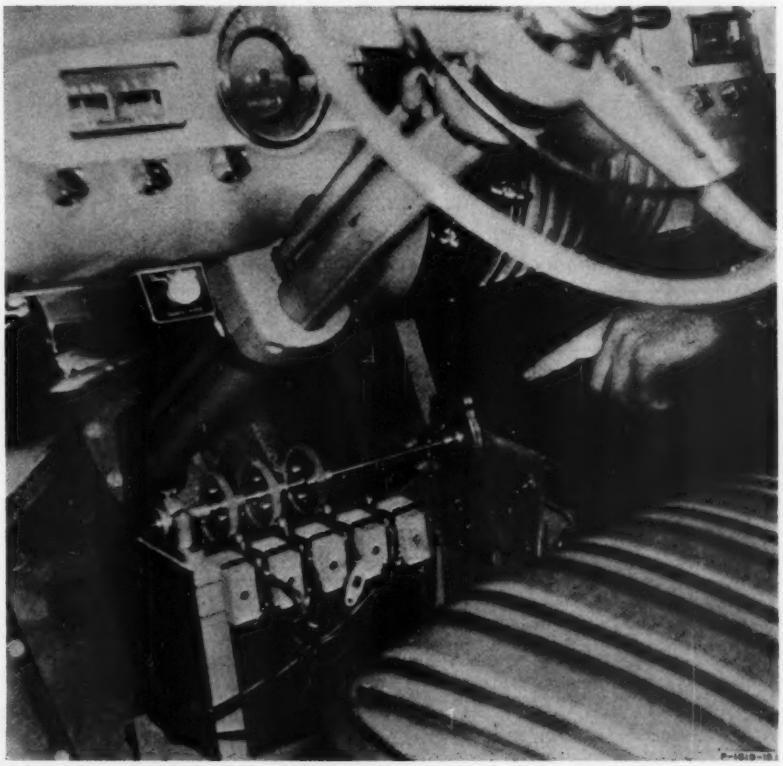

Fig. 3. View of accelerator cam and plastic cams which control sampling solenoid.

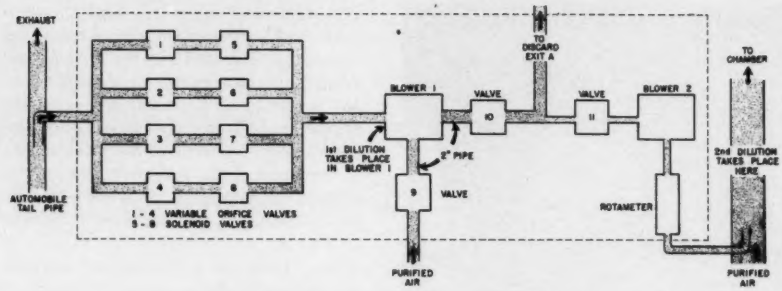

Fig. 4. Diagram of sampling and dilution system.

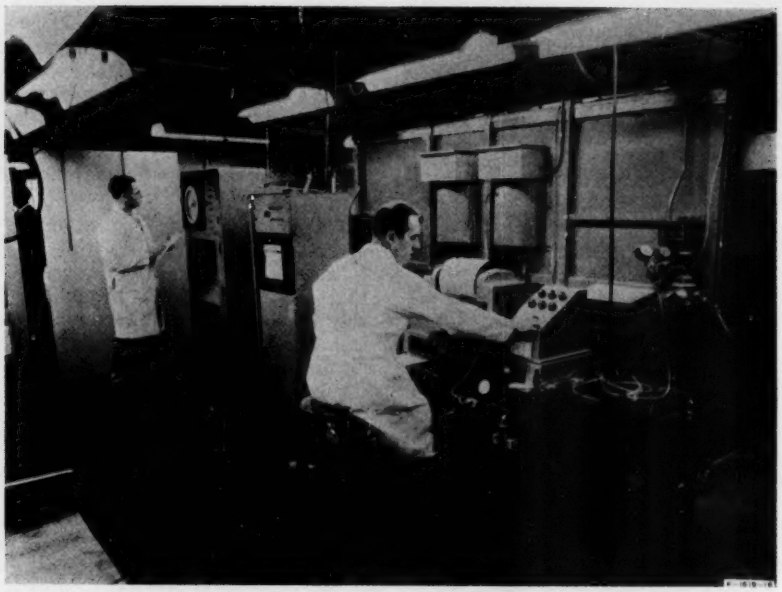

Fig. 5. View of air mixture treatment chamber and instruments.

Table I—Summary of Results on Irradiation Intensity Experiments

No. of Arcs	No. of Expts.	Hydrocarbon Content of Mixture Entering Chamber,[a] ppm	Average Eye Irritation Index (Arbitrary Units)[b]	Analysis of Selected Materials in Irradiated Mixture in Chamber at Steady State		
				Average Oxidant,[c] ppm	Average Nitrogen Dioxide,[d] ppm	Average Carbon Monoxide,[e] ppm
0	1	4.8	1	0	0.02	109
6	2	5.3	2	0.13	0.19	85
12	2	5.6	10	0.44	0.37	109
24	3	6.2	16	0.58	0.34	97

[a] Determined by a Perkin-Elmer Model 21 Spectrophotometer equipped with a 10-meter cell; sample was passed through Drierite, pressurized to 100 lb, and read at 3.4 μ; calibration was made with hexane; precision estimated at ±15 percent.

[b] Average of 20 reports of 10 subjects reporting after each of two exposures; precision estimated at ±20 percent.

[c] Determined by a recording colorimeter with potassium iodide reagent; precision estimated at ±15 percent.

[d] Determined by a recording colorimeter with Saltzman's reagent; precision estimated at ±15 percent.

[e] Determined by a Mine Safety Appliance LIRA infrared analyzer; precision estimated at ±10 percent.

was conducted to investigate the half life of the irritant. The decay rates of oxidant and nitrogen dioxide were determined at the same time.

The exhaust-air mixture, temperature, and residence time were the same for this series of experiments as for the irradiation intensity experiments previously described. The contents of the chamber were brought, first, to a steady state of irradiation with continuous flow of the exhaust-air mixture and then the flow was shut off for varying lengths of time to achieve a static state. Experiments 2, 4, 6, and 7 were conducted in the dark; experiments 1, 3, 5, and 8 were conducted with additional irradiation from all 24 mercury lamps. The experimental results summarized in Table II show a small decrease in eye irritation at the 0.5-hour dark static state, but little further change at greater lengths of static time up to 3.5 hours (experiments 2, 4, 6, and 7). Thus the 15-second delay in passing the mixture from chamber to eye mask has little if any effect in the degree of eye irritation. The use of irradiation appeared to have little effect on the half life of the eye irritant (experiments 1, 3, 5, and 8). The decay rates of both the oxidant and nitrogen dioxide levels were rapid compared with the half life of the eye irritant. The initial decay rate of the oxidant was apparently unaffected by irradiation; its half life was 0.5 to 1.0 hour. The initial decay rate of the nitrogen dioxide was increased by irradiation; its half life was 0.25 to 0.5 hour. The decay rates of both components were a function of time. These data indicate that the eye irritant is not measured either by the oxidant recorder or by the nitrogen dioxide.

Since little decrease occurred in the eye irritation index with 3.5 hours of static operation, additional experiments 9, 10, 11, and 12 were conducted with a static time of 24 hours. During these experiments, the half life of the irritant was found to be affected by the circulation of the mixture within the chamber and for this reason circulation time was varied. The results are summarized in Table III. The half life of the eye irritant without circulation of the chamber contents was about 24 hours while the half life of the eye irritant with circulation was estimated to be about 12 hours.

The effect of chamber leakage on the half life of the eye irritant and on the decay rates of oxidant, nitrogen dioxide, and carbon monoxide was ignored since the decrease in hydrocarbon and carbon monoxide values in the mixtures within the chamber during these 24-hour static state experiments was about 10 percent.

Summary

Both the reported degree of eye irritation and the values of the oxidant

Fig. 6. Subject wearing eye mask and respirator.

Table II—Summary of Results on the Half-Life Experiments[a]

Expt. No.	Phase A: Steady State Values, Oxidant, ppm	Phase A: Steady State Values, Nitrogen Dioxide, ppm	Phase B: Length of Static State, hr	Phase B: Amount of Additional Irradiation (No. of Arcs)	Phase B: Values at End of Static State, Eye Irritation Index (Arbitrary Units)	Phase B: Values at End of Static State, Oxidant, ppm	Phase B: Values at End of Static State, Nitrogen Dioxide, ppm
1	0.59	0.28	0	24	16	0.59	0.28
2	0.55	0.33	0.5	0	13	0.29	0.20
3	0.65	0.35	0.5	24	16	0.34	0.08
4	0.65	0.28	1.0	0	8	0.32	0.12
5	0.44	0.30	1.0	24	10	0.20	0.01
6	0.84	0.48	1.5	0	12	0.36	0.26
7	0.86	0.38	3.5	0	14	0.27	0.15
8	0.89	0.64	3.5	24	12	0.30	0.03

[a] Each experiment was conducted in two phases: the dynamic portion in Phase A, in which the exhaust-air mixture was continuously passed through the chamber and irradiated with an average residence time of 1 hr; the static portion in Phase B, in which entrance and exit ports of the chamber were closed and the exhaust-air mixture was held in the chamber for varying lengths of time with and without additional irradiation before testing for eye irritation and analysis of components. Circulation was effected with a 24-inch electric fan. See Table I for methods of analysis.

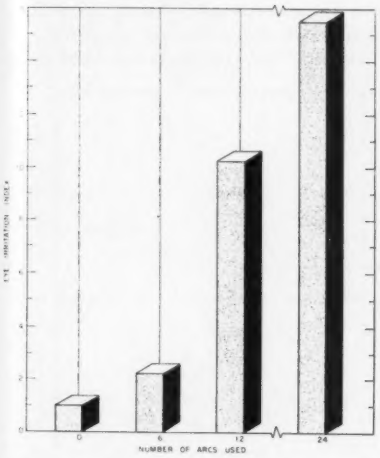

Fig. 7. Eye irritation as a function of irradiation intensity.

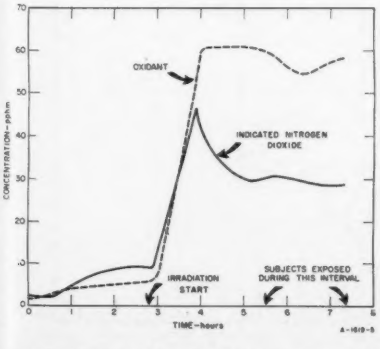

Fig. 8. Typical traces of oxidant and indicated nitrogen dioxide during experiments resulting in eye irritation 24-arc irradiation.

and nitrogen dioxide in the exhaust-air mixtures were found to vary directly with the irradiation intensity.

The half life of the eye irritant was found to be about 24 hours, as measured by a panel of 10 human subjects. The decay rates of the oxidant and nitrogen dioxide under static state conditions were shown to be direct functions of time, as measured by recording instruments. During the static state experiments, the decay rates indicated a half life of less than one hour for oxidant and less than 0.5 hour for nitrogen dioxide. The oxidant decay was independent of additional irradiation; the nitrogen dioxide decay was increased by additional irradiation.

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Table III—Summary of Results from the Half-Life Experiments at a 24-hour Static State[a]

Expt. No.	Phase A: Steady State Values, Oxidant, ppm	Phase A: Steady State Values, Nitrogen Dioxide, ppm	Phase B: Amount of Circulation Time, hr	Phase B: Values at End of Static State, Eye Irritation Index (Arbitrary Units)	Phase B: Values at End of Static State, Oxidant, ppm	Phase B: Values at End of Static State, Nitrogen Dioxide, ppm
9	0.66	0.31	24	5	0.09	0.03
10	0.70	0.35	12	8	0.08	0.01
11	0.66	0.34	0	7	0.09	0.03
12	0.65	0.26	0	10	0.13	0.00

[a] Each experiment was conducted in two phases: the dynamic portion in Phase A, in which the exhaust-air mixture was continuously passed through the chamber and irradiated with an average residence time of one hour; the static portion in Phase B in which entrance and exit ports of the chamber were closed and the exhaust-air mixture was held in the chamber for 24 hours with and without circulation before testing for eye irritation and analysis of components. Circulation was effected with a 24-inch electric fan. See Table I for methods of analysis.

Role of the Meteorological Engineer in COMMUNITY AIR POLLUTION SURVEYS*

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All aspects of air pollution should first be subjected to meteorological analysis before any other phase of the investigation is undertaken. Although this statement is axiomatic to the meteorological engineer, it seems necessary to demonstrate it to everyone associated with an air pollution problem. Perhaps it is the relative newness of the science or the lack of understanding of the programs' directors, but no matter what the reason the situation exists. It is the aim of this paper to mention a few of the ways in which meteorology can lay the groundwork for a complete analysis of a pollution situation. The advantages of starting with a meteorological investigation can best be realized by illustrating the procedures involved in establishing this basic background. Initially, a broad understanding of the general situation is obtained from standard climatology with the usual parameters of temperature, precipitation, visibility, winds, and cloudiness. This first study helps determine which parameter, or group of parameters, should be investigated more fully in terms of a specialized climatology.

This specialized climatology re-examines the data toward pinpointing the parameters in need of "on the spot" investigation. This sets the stage for field operations. Having determined the most critical times for pollution measurements from the previous analyses, the meteorological engineer can conduct the field operations knowing that he can make optimum use of the resultant data. When the final analysis is completed, recommendations can then be made for all other phases of the program. The scope of the meteorological analysis varies somewhat with the magnitude of the problem; however, the resulting benefits from this analysis are such as to make consideration of scope of secondary importance. The cost will always be small when compared with the ultimate value.

Standard Climatology

The basic information derived from standard compilations usually consists of arithmetic means of the temperature, precipitation, visibility, cloudiness, and wind speed with wind roses for direction. From the pollution standpoint, certain inferences can be made from these parameters. In the following, each item is discussed separately although it becomes obvious that overlapping is unavoidable.

a. Temperature

The mean monthly temperature and the mean range, average dewpoint, and humidity are important in identifying

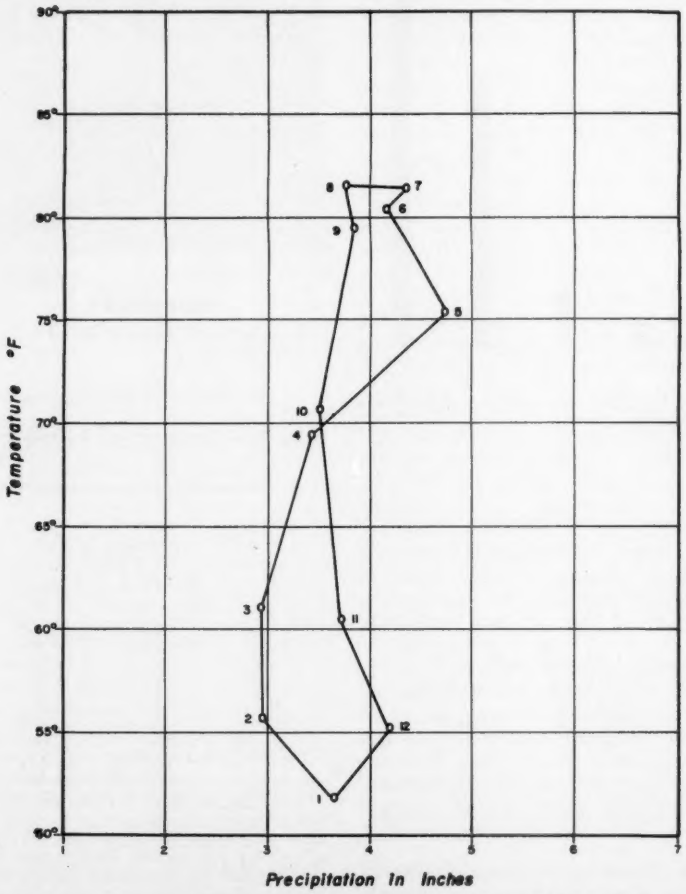
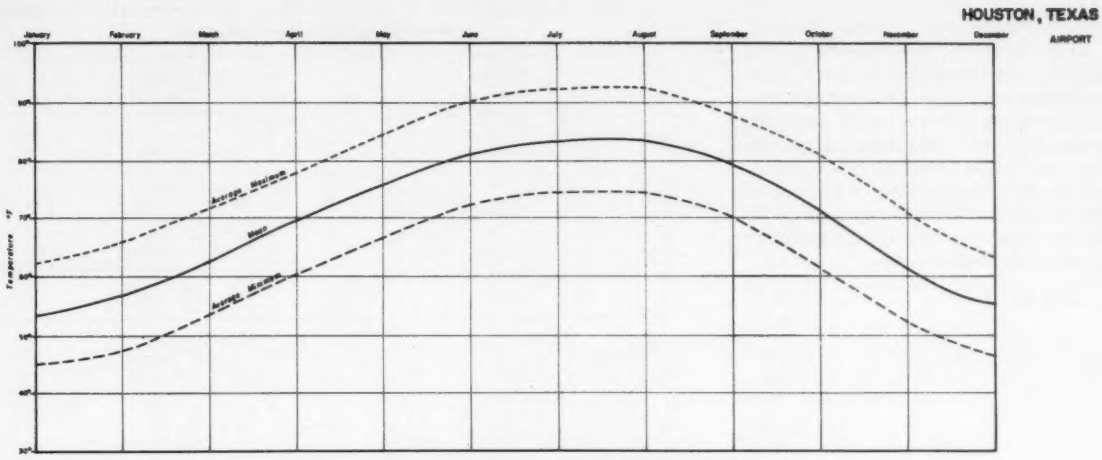
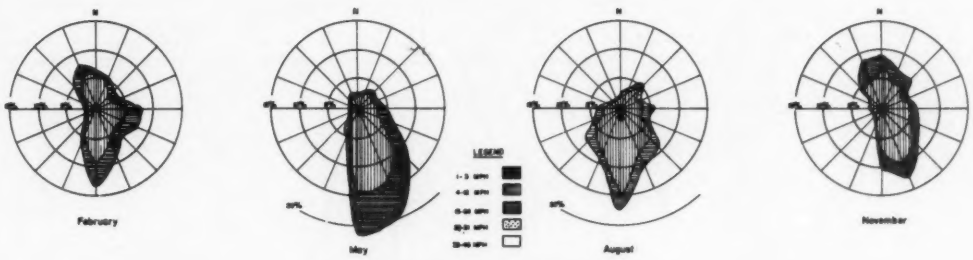


Fig. 1. Climagram for Houston, Texas (airport). Period of record, 1905–1955.

* Presented at the 51st Annual Meeting of the Air Pollution Control Association held at the Hotel Sheraton, Philadelphia, Pa., May 25–29, 1958.



ANNUAL VARIATION OF TEMPERATURE

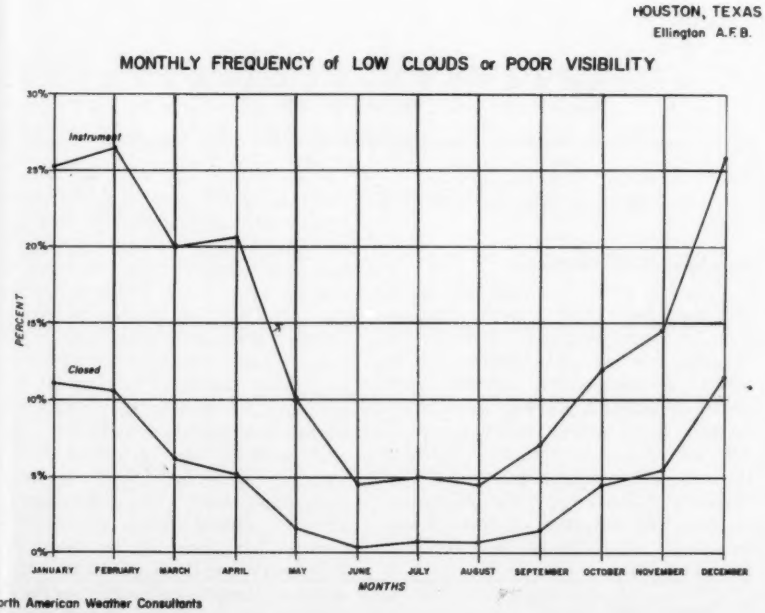


WIND ROSES FOR SELECTED MONTHS

North American Weather Consultants

Wind Data for Ellington A.F.B.

Fig. 2.



North American Weather Consultants

Fig. 3.

air mass influences, especially when coupled with precipitation. One method of graphically portraying the course of these influences is the Climagram for Houston, Fig. 1. This particular area provides an example of continentality with relatively even precipitation amounts throughout the year and fairly wide temperature range. The temperature range is amplified by plotting the mean maxima and minima by month and noting the yearly variation, Fig. 2. A more interesting aspect of temperature averages occurs if there happens to be a rasonde station within the considered area. Averages by specified levels can furnish enough information to not only fix the air mass types more positively but also indicate whether or not a low level inversion is sufficiently characteristic of the region to be reflected in the mean. By assuming classic stability characteristics of air masses, and knowing the major air masses influencing the area, a general knowledge of stability characteristics of the region of interest can be obtained.

b. Precipitation

Aside from the identification of climatic type as illustrated by the Climagram (above), precipitation averages can be informative in terms of the cleansing action of rainfall. The mean number of days per month of precipitation can in themselves determine which months of the year will be most likely to have the least amount of pollution through virtue of maximum washout.

c. Visibility

Although a relatively crude measure as precision measurements go, visibility offers one of the best indications of atmospheric pollution. Obviously, the greater the aerosol density, the greater the decrease in visibility. The months that show a low mean visibility are therefore a priori suspect as months of greatest pollution. The actual obscurant may, of course, be strictly natural such as precipitation, haze, or fog, but if nothing else, the existence of a mean low visibility value indicates a persistence of obscuring elements and hence a large probability of stable conditions—a prerequisite for all pollution regimes. An additional source of data is the type of compilation made particularly for aviation. If such is available for the region of interest, considerable information pertinent to pollution can be gleaned. For example, Fig. 3 shows the range of percent occurrence of low clouds and/or poor visibility by month for the entire year for Ellington AFB, while Fig. 4 shows the diurnal variation. If one would take this as an indicator of stability, then the obvious conclusion is that the summer months should be relatively free from pollution since it shows a decided minimum of low cloud and/or obscuration.

d. Winds

Wind data are usually presented in the form of wind roses with frequency indicated by various devices such as lengths of arrows, widths of arrows, etc. The pertinent information for pollution problems is unfortunately fairly well obscured by the averaging systems. However, the mean values such as average wind speeds and prevailing direction are helpful to the extent that they further aid in defining air mass influences.

e. Cloudiness

The amount of cloudiness, even when broken down into categories of partly cloudy, cloudy, and clear are not of great aid except as a general guide. A high percentage of cloudiness for any particular month could infer a persistence of stratus condition, if the station is located near a large body of water, or conversely, a high percentage of clear (sunshine) indicates great insolation with the resultant thermal turbulence inferring large scale diffusion of pollutants.

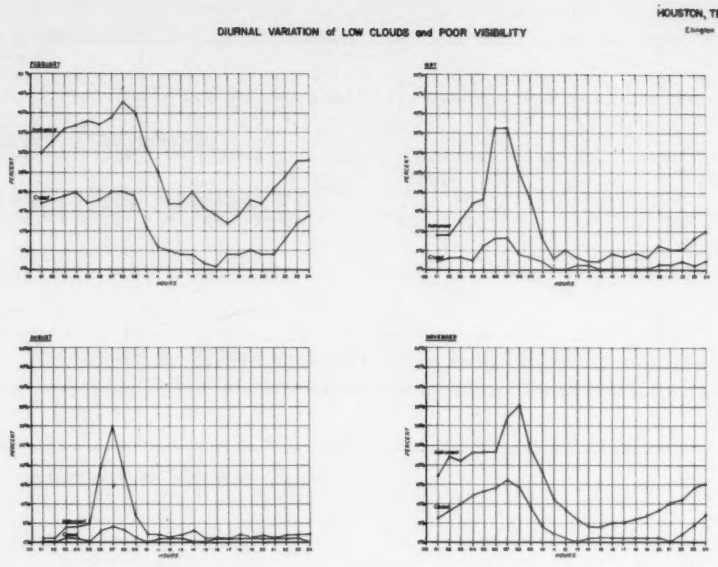


Fig. 4

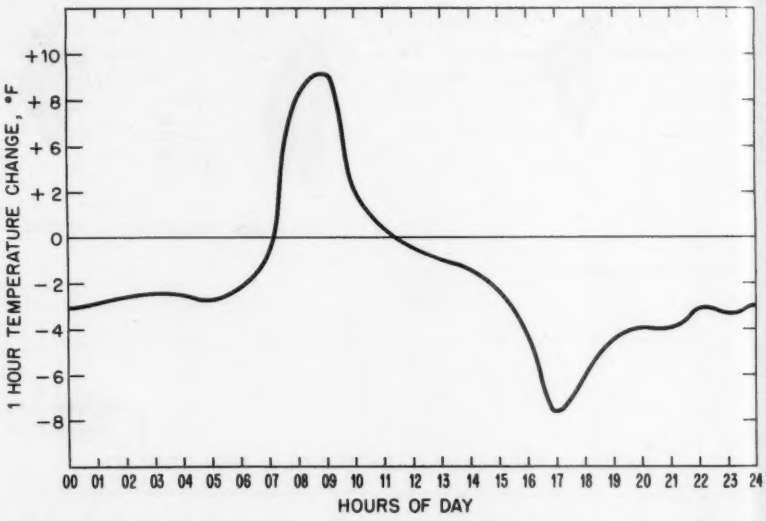


Fig. 5. January hourly temperature change during periods of light winds, Santa Barbara, California.

Specialized Climatology

With the general climatology made up from individual hourly observations, it becomes highly desirable to examine the raw data objectively in terms of compilations directly pertinent to pollution problems. This can be done fairly readily once a grasp of the end product is obtained. Taking the same parameters as discussed in the Standard Climatology, the following analyses are indicative of some of the techniques available to the meteorological engineer.

a. Temperatures

One approach to the problem of the duration of the transition period between early morning stability and thermal instability resulting from insolation is to take the rate of temperature change per hr. It was found, for example, that at Santa Barbara in January the hourly rate took a large jump shortly after sunrise and a decided drop near sunset. These values were obtained by averaging each hourly change of temperature by hr per month and plotting the resultant hourly means. Fig. 5 illustrates the results of this computation. This method is most effective during relatively front-free periods, but these can be determined from examining the hourly data. In essence, the large jump after sunrise establishes the time interval during which fumigation conditions could take place.

Table I—Monthly Relative Percentage of Wind Speed Ranges with Precipitation Types

	JANUARY				FEBRUARY			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	—	36	48	16	—	32	54	12
R–[a]	—	54	45	—	—	41	58	1
R	—	50	50	—	—	67	33	—
RW–	—	31	62	6	2	36	56	7
RW	—	—	100	—	—	22	78	—
L	1	54	43	1	3	57	40	—
F/GF	6	80	14	—	12	73	15	—
K/H	5	72	23	—	8	69	23	—
ZP	—	51	49	—	—	25	75	—

	MARCH				APRIL			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	—	33	64	3	4	28	60	9
R–	1	29	65	5	—	36	56	7
R	—	33	67	—	—	100	—	—
RW–	—	32	59	9	2	23	67	9
RW	—	100	—	—	—	78	22	—
L	3	56	40	1	3	68	29	—
F/GF	10	72	18	—	9	70	20	—
K/H	4	61	35	—	7	78	15	—
ZP	—	—	—	—	—	—	—	—

	MAY				JUNE			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	—	27	67	6	—	50	49	1
R–	2	37	61	—	—	40	60	—
R	—	—	100	—	—	—	—	—
RW–	1	37	59	4	3	54	42	1
RW	—	100	—	—	—	27	64	9
L	—	57	43	—	—	—	—	—
F/GF	12	82	6	—	18	79	3	—
K/H	9	71	19	—	6	65	28	—
ZP	—	—	—	—	—	—	—	—

	JULY				AUGUST			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	6	55	39	—	1	64	31	3
R–	11	70	19	—	8	73	19	—
RW–	1	60	39	—	8	77	15	—
RW	—	25	75	—	—	50	50	—
L	—	—	—	—	—	—	—	—
F/GF	23	77	—	—	22	78	1	—
K/H	9	88	3	—	9	87	4	—
ZP	—	—	—	—	—	—	—	—
R	—	—	—	—	—	—	100	—

	SEPTEMBER				OCTOBER			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	3	53	44	—	—	38	57	5
R–	1	64	34	1	3	43	48	6
RW–	1	73	22	2	1	51	45	3
RW	—	60	40	—	—	92	8	—
L	—	100	—	—	—	56	44	—
F/GF	15	82	3	—	14	82	4	—
K/H	4	86	10	—	3	71	26	—
ZP	—	—	—	—	—	—	—	—
R	—	—	100	—	—	8	77	15

	NOVEMBER				DECEMBER			
	0–3	4–12	13–24	>25	0–3	4–12	13–24	>25
T	—	23	65	12	5	38	52	5
R–	4	42	53	1	4	46	49	1
RW–	—	31	59	10	1	31	62	6
RW	—	12	75	12	—	33	50	17
L	8	45	47	—	9	70	20	—
F/GF	11	75	14	—	14	73	12	—
K/H	6	60	34	—	9	73	18	—
ZP	—	—	—	—	—	—	—	—
R	—	67	33	—	11	22	67	—

[a] R– = Light rain. R = Moderate rain. RW– = Light rain showers. RW = Moderate rain showers. L = Drizzle. T = Thunderstorm. F/GF = Fog, ground fog. K/H = Smoke, haze. ZP = Freezing Precipitation.

The interval near sunset represents the probable transition between looping and lofting plume types.

As far as temperature alone is concerned, the most valuable information is obtained from vertical soundings. If they are available reasonably close to the area, an examination of the low level temperature profiles will provide the thermal stability information. Compilations of stability indices for various seasons will provide a working knowledge of the frequency of stable regimes.

b. Precipitation

Although the Standard Climatology establishes the mean monthly precipitation, the linkage between precipitation and pollution requires a more complex relationship. It is necessary, therefore, to delineate precipitation in the forms most convenient for inputs in pollution analysis equations. These forms are essentially types of precipitation, size of hydrometeors, duration of precipitation and wind analysis for specifications. The following charts and tables are examples of these items in usable forms. Table I shows the relative frequency of specified wind speed ranges with the various precipitation types.

The actual pollution washout is determined on the basis of particle sizes involved and intensities and durations of the precipitation types. Since it can be demonstrated that the larger the particle and the heavier the precipitation the greater the percentage removed from the atmosphere per unit time, it is possible to determine the RP (Residual Pollution) factor for any type of precipitation once the particle size of the pollutant is known. In the selection of the appropriate equations, it was essential to determine first the dominant mechanism by which the particulate matter was removed by the precipitation elements. The five major hypotheses concerned with this mechanism are:

1. Particle inertia. Impaction of the particle and droplet. This occurs when the particle trajectory departs from the aerodynamic flow around the precipitation droplets because of inertia and impinges upon this droplet.
2. Interception occurs when the particle center follows the aerodynamic flow around the droplet but the edges of the two bodies intersect and adhesion results.
3. Electrostatic attraction.
4. Random molecular motion or Brownian Diffusion (Agglomeration).
5. Activity of particulate matter is condensation nuclei.

Of these five, (1 above) impaction of the particle and droplet provides the

mechanism by which most of the washout occurs. However, this requires the determination of the drop number and size distribution as related to rainfall intensity, as well as the collection-efficiency for the various drop and pollutant particle sizes.

Best[1] has given a distribution which fits the experimental data reasonably well if one uses a mean distribution of the drop size over time or space, so that the transients (large drops at the onset of a precipitation cell and small drops as it leaves), may be averages. Also, the precipitation must be of a non-orographic type which yields significantly different drop size distribution.[2] Since, in the example we are dealing with time intervals of one half hour or greater and a country of flat terrain, Best's distribution was considered adequate.

Fig. 6 (*see pages 317, 318, 319*) extends Chamberlain's curves,[3] to higher precipitation intensities, based on the same functions relating the values of fraction of pollutant removed per second to rainfall rates. In addition, rough estimates of the values of fraction of pollutant removed per second for pollutant particles of less than 2 mμ radius are given. These curves are also labeled. The terminal velocities (Vt), in cm per second, are given by Stokes Law which Chamberlain[3] has related to the collection efficiency.

From these data, Fig. 7 has been developed relating the recent Fraction of Residual Pollution to particle size for several precipitation intensities.

The particle size range of 0.1 mμ to 20 mμ radius was chosen for the following reasons:

1. Above about 20 mμ radius fall out begins to be more important than washout.
2. Below 0.1 mμ radius agglomeration begins to be of importance.

From Fig. 7 we see that the collection efficiencies are effectively zero as one approaches radii of 0.1 μ and approach constant values on the other end of the range near 20 μ.

It is also feasible to compute Residual Fraction of Pollution one mile downstream from a source region based on precipitation intensity, wind speed, and particle size. For this we turn to definitions of the various precipitation types in terms of intensity, Table II.

The precipitation types are as shown above.

The computed curves and tables have all been established for the particular case of a pollution particle of unit density.

The climatology of the percentage of Residual Pollution after precipitation, RP Climatology, is concerned with the application of theoretical computations

Precipitation Types

Type	Symbol	Range of Intensity, in./hr	Assumed Range, in/hr
Drizzle	L	0.00–0.01	0.005
Light rain	R−	0.00–0.10	0.01–0.10
Light rain showers	RW−	0.00–0.10	0.01–0.10
Moderate rain	R	0.10–0.30	0.10–0.30
Moderate rain showers	RW	0.10–0.30	0.10–0.30
Heavy rain	R+	0.30–	0.30–0.70
Heavy rain showers	RW+	0.30–	0.30–0.70

Table II—Fraction of Residual Pollution after Travel One Mile Downstream from a Source During Different Precipitation Types and Wind Speeds (U)

Particle Radius	Type Precip.	One-Hour Residual Fraction	Miles per Hour 3	5	10	15	20	30	40
			3	4	8	12	17	25	34 ≅
2μ	L	0.999	0.9997	0.9999	—	—	—	—	—
	R−	0.866	0.953	0.972	0.988	0.991	0.993	0.995	0.996
	RW−	0.859	0.951	0.970	0.985	0.990	0.992	0.995	0.996
	R	0.615	0.844	0.903	0.951	0.967	0.975	0.983	0.987
	RW	0.599	0.843	0.902	0.950	0.966	0.975	0.983	0.987
	R+	0.330	0.691	0.801	0.895	0.929	0.946	0.964	0.973
	RW+	0.298	0.668	0.785	0.886	0.922	0.941	0.960	0.970
6 μ	L	0.986	0.995	0.972	0.9986	0.9990	0.9993	0.9995	0.9999
	R−	0.423	0.751	0.842	0.918	0.946	0.956	0.972	0.979
	RW−	0.313	0.679	0.793	0.890	0.925	0.944	0.962	0.971
	R	0.073	0.417	0.592	0.769	0.840	0.940	0.916	0.937
	RW	0.032	0.316	0.501	0.708	0.794	0.841	0.891	0.917
	R+	0.004	0.154	0.326	0.571	0.688	0.756	0.830	0.869
	RW+	0.0009	0.098	0.248	0.498	0.629	0.706	0.793	0.840
10 μ	L	0.978	0.993	0.996	0.998	0.9985	0.9989	0.9993	0.9994
	R−	0.364	0.714	0.817	0.904	0.935	0.951	0.967	0.975
	RW−	0.239	0.621	0.751	0.867	0.909	0.931	0.953	0.965
	R	0.047	0.360	0.542	0.736	0.815	0.858	0.903	0.926
	RW	0.018	0.262	0.448	0.669	0.765	0.818	0.875	0.905
	R+	0.002	0.123	0.284	0.533	0.658	0.730	0.811	0.855
	RW+	0.0002	0.061	0.188	0.433	0.572	0.658	0.756	0.811
20 μ	L	0.970	0.990	0.994	0.997	0.9980	0.9985	0.9990	0.9992
	R−	0.325	0.688	0.799	0.894	0.928	0.945	0.963	0.972
	RW−	0.200	0.585	0.725	0.851	0.898	0.923	0.948	0.961
	R	0.035	0.328	0.512	0.751	0.800	0.846	0.894	0.920
	RW	0.011	0.224	0.407	0.638	0.741	0.799	0.861	0.894
	R+	0.0009	0.097	0.247	0.497	0.628	0.705	0.792	0.840
	RW+	0.0001	0.045	0.156	0.314	0.1538	0.629	0.734	0.793

Form of Interpolating and Extrapolating Equation:

$$\text{Log } F = -A/U \qquad \text{or } \text{Log}(-\text{Log } F) = -\text{Log } U + C$$

Table III—Climatological Table of Residual Pollution for Houston, Tex.

Fractional RP, Particle Radius, μ				Duration, hr	Monthly Precipitation Regime, Percentages											
2	6	10	20		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Light Rain																
0.866	0.423	0.364	0.325	1	1.0	0.8	1.1	0.9	0.4	0.3	0.3	0.1	0.2	0.2	0.5	0.8
0.750	0.179	0.132	0.106	2	0.8	1.0	0.9	0.5	0.4	0.2	0.1	0.1	0.1	0.2	0.2	0.5
0.650	0.076	0.048	0.034	3	0.5	0.4	0.5	0.1	0.3	—	0.3	—	—	0.4	0.2	0.4
0.563	0.032	0.018	0.011	4	0.4	0.4	0.4	0.7	0.4	—	—	0.3	—	0.1	0.3	0.3
0.488	0.014	0.006	0.004	5	0.2	0.7	0.2	0.5	—	—	0.2	0.2	0.3	0.2	0.2	0.3
0.238	<0.0001	<0.0001	<0.0001	10	0.5	1.3	0.7	0.7	—	0.6	0.2	—	0.6	0.5	0.4	0.3
0.116	<0.0001			15	—	0.5	0.5	—	—	—	—	—	—	0.9	0.4	—
0.057				>20	—	—	0.8	0.7	—	—	—	—	1.3	—	0.6	1.2
Moderate Rain																
0.615	0.073	0.047	0.035	1	—	—	—	0.1	—	—	0.2	0.1	0.1	—	—	—
0.379	0.005	0.002	0.001	2	—	—	—	—	—	—	—	—	—	—	—	—
0.233	>0.0001	>0.0001	<0.0001	3	—	—	—	—	—	—	—	—	—	—	—	0.1
0.143	<0.0001	<0.0001		4	—	—	—	—	—	—	—	—	—	—	—	—
0.088				5	—	—	—	—	—	—	—	—	—	0.2	—	—
0.008				10	—	—	—	—	—	—	—	—	—	—	—	—
<0.001				15	—	—	—	—	—	—	—	—	—	—	—	—
<0.0001				>20	—	—	—	—	—	—	—	—	—	—	—	—
Heavy Rain																
0.330	0.004	0.002	<0.001	1	—	—	—	—	—	—	—	—	—	0.1	—	—
0.109	<0.0001	<0.0001	<0.0001	2	—	—	—	—	—	—	—	—	—	—	—	—
0.036				3	—	—	—	—	—	—	—	—	—	—	—	—
0.012				4	—	—	—	—	—	—	—	—	—	0.1	—	—
0.004				5	—	—	—	—	—	—	—	—	—	—	—	—
<0.0001				10	—	—	—	—	—	—	—	—	—	—	—	—
				15	—	—	—	—	—	—	—	—	—	—	—	—
				>20	—	—	—	—	—	—	—	—	—	—	—	—
Light Rain Showers																
0.859	0.313	0.239	0.200	1	0.5	0.7	0.5	0.6	0.9	0.8	1.3	0.7	1.4	0.5	0.7	0.6
0.739	0.098	0.057	0.040	2	0.8	0.4	1.0	0.7	0.4	0.4	0.9	0.5	0.8	0.4	0.5	0.5
0.635	0.030	0.014	0.008	3	0.1	—	0.4	0.4	0.4	0.4	0.6	0.1	0.8	0.1	0.1	0.4
0.546	0.010	0.003	0.002	4	—	—	0.4	0.4	0.2	0.6	0.3	0.5	0.6	0.4	0.1	—
0.469	0.003	<0.001	<0.0001	5	0.2	0.2	—	—	0.2	—	—	0.2	—	—	0.2	0.3
0.220	≪0.0001	≪0.0001	≪0.0001	10	0.4	0.6	0.4	0.4	—	1.1	0.2	—	—	0.5	0.2	0.4
0.103				15	—	0.6	—	—	—	—	—	—	—	—	—	—
0.048				>20	—	—	—	—	—	—	—	—	—	0.7	—	—
Moderate Rain Showers																
0.599	0.032	0.018	0.011	1	0.1	0.1	—	0.1	0.1	0.3	—	—	0.2	0.1	—	0.1
0.358	0.001	>0.0001	>0.0001	2	0.2	0.2	—	0.1	—	0.1	—	—	—	—	0.1	—
0.214	<0.0001	<0.0001	≪0.0001	3	—	—	—	—	—	—	—	—	—	0.1	—	—
0.128				4	—	—	—	—	—	—	—	—	—	—	—	—
0.077				5	—	—	—	—	—	—	—	—	—	—	—	—
0.006				10	—	—	—	—	—	—	—	—	—	0.3	—	—
≪0.001				15	—	—	—	—	—	—	—	—	—	—	—	—
≪0.0001				>20	—	—	—	—	—	—	—	—	—	—	—	—
Heavy Rain Showers																
0.230	<0.001	>0.0001	<0.0001	1	—	—	0.1	0.1	—	0.1	—	—	—	—	0.1	0.1
0.089	≪0.0001	≪0.0001		2	—	—	—	0.1	—	—	—	—	—	—	—	—
0.026				3	—	—	—	—	—	—	—	—	—	—	—	—
0.008				4	—	—	—	—	—	—	—	—	—	—	—	—
0.002				5	—	—	—	—	—	—	—	—	—	—	—	—
≪0.0001				10	—	—	—	—	—	—	—	—	—	—	—	—
				15	—	—	—	—	—	—	—	—	—	—	—	—
				>20	—	—	—	—	—	—	—	—	—	—	—	—

of washout to statistical compilations of precipitation climatology. We see from the compilations of precipitation regimes, Table III, that there exist definite seasonal trends in lengths of periods of precipitation as well as the occurrence of precipitation itself. From the tables of computations on RP we obtained values to apply to these various regime periods and wind speeds. These combined tables facilitate estimation of RP factor on a climatological basis for a relatively large range of particle sizes.

The combination of computations based on wind speeds and the table of relative percentages of occurrence of precipitation types of various wind speed brackets provides relative frequency values as shown in Table IV.

In summary, then, we now have at hand the figures which will provide the answers to the effect of precipitation on pollution and the probable frequency of this effect in alleviating pollution regime.

Visibility

One set of theoretical results which have been found to be of direct and immediate application to surveys are the relationships between the particulate matter suspended in the atmosphere, the relative humidity, and the visibility.

According to the U. S. Weather Bureau definition: "Visibility is a term that denotes the greatest distance an object of specified characteristics can be seen and identified." Although the term is generally considered a very poor one for the purpose, it is so well established by convention that attempts to substitute a more appropriate term seem to serve only to compound the confusion. In essence, the reported visibility will depend on the initial contrast between the target and its background, the threshold value at which the particular observer can just detect or recognize the contrast, and the attenuation of contrast by the gases and suspensoids in the atmosphere between the observer and the target. This attenuation of contrast by the intervening aerosol (by which we mean the gaseous constituents and the suspended matter) is to a small extent governed by molecular scattering of light by the gaseous constituents, but largely governed by the solid and liquid particles in suspension.

The amount of attenuation will depend both on the size distribution of these suspensoids and on the number. The number of particles is independent of the relative humidity, and the relative humidity at which dry particles undergo a phase transition and become liquid droplets is a function of the physical and chemical structure of the particles. For example, sea salt

Table IV—Climatological Table of Residual Pollution for Houston, Tex.

Fractional RP, Particle Radius, μ				Wind Speed, knots	Monthly Wind Speed Range, Relative Percentages											
2	6	10	20		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Light Rain																
0.866	0.423	0.364	0.325	>0–3	—	—	1	—	2	—	11	8	1	3	4	4
0.953	0.751	0.714	0.688													
0.972	0.842	0.817	0.799	>4–12	54	41	29	36	37	40	70	73	64	43	42	46
0.991	0.946	0.935	0.928													
0.993	0.956	0.951	0.945	>13–24	45	58	65	56	61	60	19	19	34	48	53	49
0.995	0.972	0.967	0.963													
0.996	0.979	0.975	0.972	>25	—	1	5	7	—	—	—	—	1	6	1	1
Moderate Rain																
0.615	0.073	0.047	0.035													
0.844	0.417	0.360	0.328	>0–3	—	—	—	—	—	—	—	—	—	—	—	11
0.903	0.592	0.542	0.512	>4–12	50	67	33	100	—	—	—	—	—	8	67	22
0.967	0.840	0.815	0.800													
0.975	0.940	0.858	0.846													
0.983	0.916	0.903	0.894	>13–24	50	33	67	—	100	—	—	100	100	77	33	67
0.987	0.937	0.926	0.920	>25	—	—	—	—	—	—	—	—	—	15	—	—
Light Rain Showers																
0.859	0.313	0.239	0.200	>0–3	—	2	—	2	1	3	1	8	1	1	—	1
0.951	0.679	0.621	0.585													
0.970	0.793	0.751	0.725	>4–12	31	36	32	23	37	54	60	77	73	51	31	31
0.990	0.925	0.909	0.898													
0.992	0.944	0.931	0.923	>13–24	62	56	59	67	59	42	39	15	22	45	59	62
0.995	0.962	0.953	0.948													
0.996	0.971	0.965	0.961	>25	6	7	9	9	4	1	—	—	2	3	10	6
Moderate Rain Showers																
0.599	0.032	0.018	0.011	>0–3	—	—	—	—	—	—	—	—	—	—	—	—
0.843	0.316	0.262	0.224													
0.902	0.501	0.448	0.407	>4–12	—	22	100	78	100	27	25	50	60	92	12	33
0.966	0.794	0.765	0.741													
0.975	0.841	0.818	0.799	>13–24	100	78	—	22	—	64	75	50	40	8	75	50
0.983	0.891	0.875	0.861													
0.987	0.917	0.905	0.894	>25	—	—	—	—	—	9	—	—	—	—	12	17

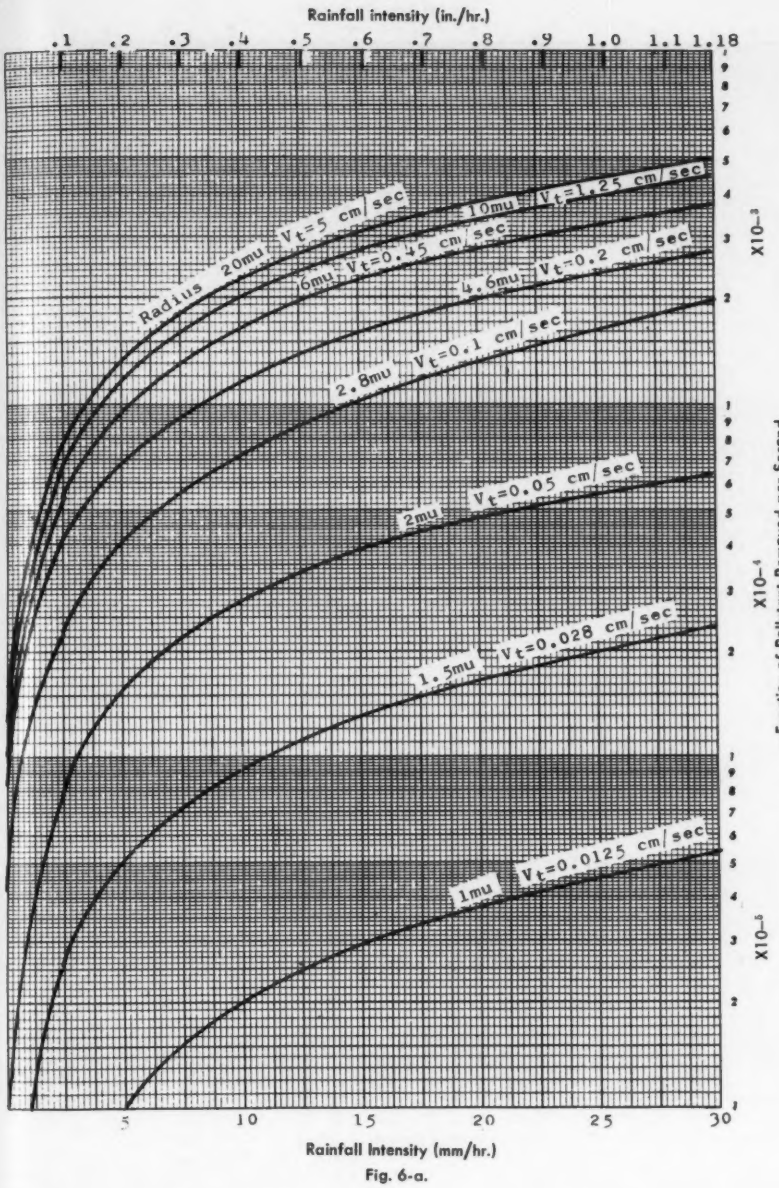


Fig. 6-a.

particles become liquid droplets and commence to grow at relative humidities of around 70% while many of the sulfate compounds do not undergo this phase transition until the relative humidity reaches 90%. The frequent existence of fogs and mists at relative humidities well below 100% is ample evidence for the existence of this phenomenon. Once the phase transition has been achieved, the liquid droplets will grow at a rate that depends on many factors, principally, the size, concentration of the salt solution, nature of the chemical substance, and the relative humidity. Thus, at a given relative humidity, the visibility is a function of the number and chemical composition of the particles suspended in the air. A considerable amount of scatter is introduced into the results by many factors, the most important of which is the variation of the contrast threshold between different observers and under different lighting conditions and utilizing targets of different lighting conditions and utilizing targets of different contrast against their background. While individual reports may be quite misleading, a large enough sample to average out these variations will generally give quite reliable information.

In analysis of the Houston and Ellington AFB data, it was of interest to determine whether the reported visibilities would show that streams of air reaching the airports from different directions would show the effect of a significantly different particulate loading, depending on the trajectory followed.

Table V represents a concentration of information gained from the statistical analysis of a total of 113,506 individual observations. For each airport separately, the punch cards were divided by relative humidity classes and each relative humidity class was subdivided according to wind direction, using the 16 point compass standard to this type of observation. Three relative humidity classes were used as follows: 60–64%, 75–79%, and 90–94%. All observations reporting precipitation in any form were excluded from the calculations, since this indicates that other factors were operating to obscure the visibility besides the ones in which we were interested.

The statistic chosen to characterize the visibility for each sub-class was the median visibility, the median being the value so chosen that 50% of the reports in that category were of higher value and 50% were lower. The average value or arithmetic mean is not a suitable statistic to use in this work because of the method of reporting visibilities, since all values of 15 miles or over are reported as being 15 miles.

Table V—Smoothed Median Visibility, Miles

Wind Direction	Houston International Airport, Relative Humidity, %			Ellington Air Force Base, Relative Humidity, %		
	60–64	75–79	90–94	60–64	75–79	90–94
N	11.3	9.6	5.5	11.0	10.0	5.9
NNE	10.3	9.0	*5.0*	11.7	10.7	6.9
NE	9.4	*8.1*	5.7	11.5	10.1	7.5
ENE	*9.2*[a]	8.6	7.0	11.3	10.4	8.1
E	10.6	9.9	9.0	11.3	10.4	9.1
ESE	11.7	11.5	10.6	12.3	11.6	9.2
SE	13.1	12.3	10.9	12.5	11.7	9.8
SSE	13.8	12.4	10.1	13.1	11.5	9.6
S	13.5	12.3	10.2	12.6	11.7	9.9
SSW	13.8	12.2	9.8	13.1	11.8	10.2
SW	14.4	11.9	10.4	12.5	11.5	9.6
WSW	13.6	12.0	10.3	12.4	11.4	10.1
W	13.3	11.6	10.1	11.5	10.9	9.4
WNW	12.9	11.9	9.1	11.4	10.6	7.8
NW	12.3	11.1	7.9	*10.4*	*9.1*	6.5
NNW	11.9	10.6	6.9	10.9	9.8	*5.6*

[a] Lowest visibility italic.

Inspection of the table provides much interesting material. For each relative humidity group, a significant reduction in visibility is noted for certain wind directions. Expressing the lowest value of the median visibility for any wind

Table VI—Worst Median Visibility in Humidity Group Expressed as a Percentage of the Best Median Visibility in That Group

Relative Humidity Group, %	International Airport	Ellington AFB, %
60–64	64	79
75–79	65	84
90–94	46	58

direction within a given relative humidity as a fraction of the highest value calculated for that humidity group we have the following percentage reductions for the two airports as shown in Table VI.

Since we have removed the effect of relative humidity by our previous selection process, we can only conclude that this reduction in visibility is due to the

Table VII—Wind Direction and Median Visibility for Worst Wind Direction

Relative Humidity Group, %	International Airport		Ellington AFB	
60–64	ENE	9.2 mi.	NW	10.4 mi.
75–79	NE	8.1 mi.	NW	9.1 mi.
90–94	NNE	5.0 mi.	NNW	5.6 mi.

(Note that wind direction is direction from which the wind blows.)

increase in the particulate loading of the air streams as they reach the airports from certain directions.

Table VII has been prepared to show the wind direction and median visibility for the lowest visibility value determined at each airport, for each humidity group.

It is of great significance that in each case, the worst visibilities come with winds that have blown over the industrial district before arriving at the airports. It should be noted that in such streams, the visibility is invariably worse at the International Airport than it is at Ellington AFB, while a glance at Table V shows that in the case of southerly winds, for the same wind direction and the same relative humidity group, Ellington usually shows a slightly reduced median visibility. This is entirely consistent with the expected effect since the International Airport is closer to the major industrial area while Ellington is closer to the major source of natural pollutants: sea salt nuclei. Although it is possible that some slight effect of the Texas City industrial area could be detected, it is by no means a strong enough effect to be significant.

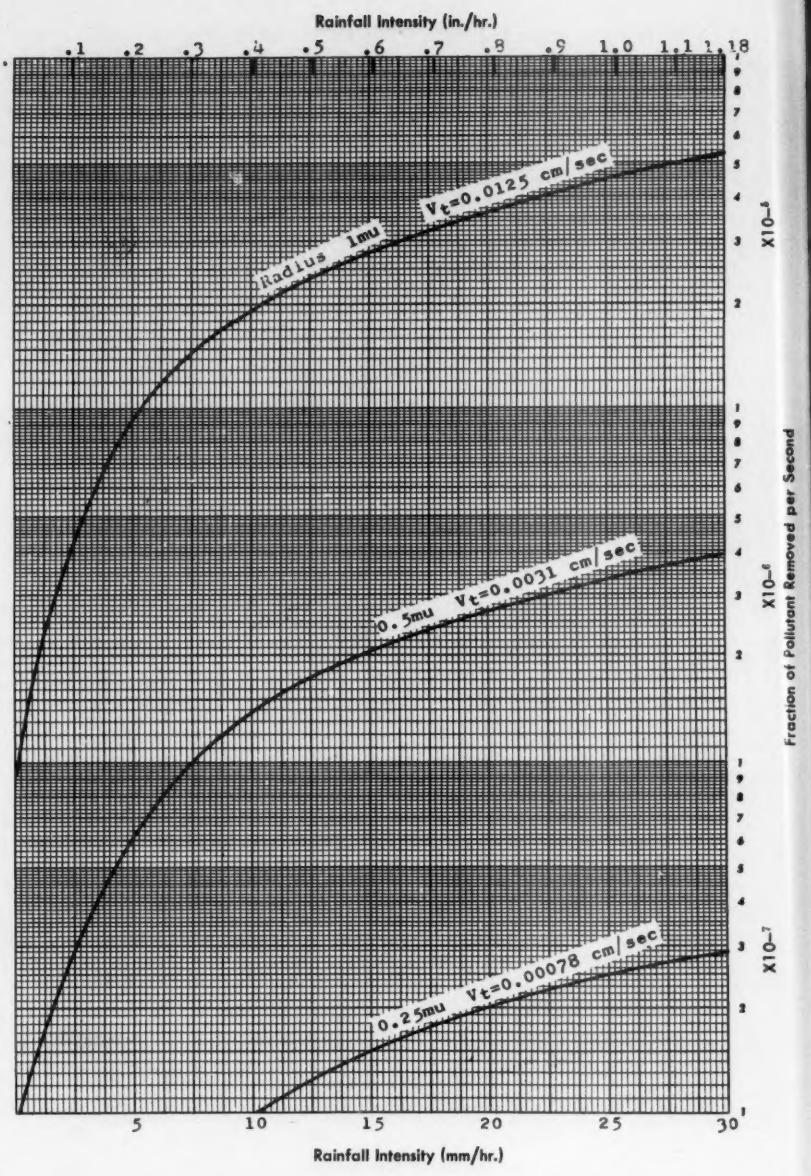


Fig. 6-b.

It must be emphasized that the conclusion drawn from these data are entirely tentative. However, this information is important since it confirms the utility of using reported visibility readings as a measure of the diffusion efficiency, thus making available for further study a large mass of historical data which can be used with a high degree of confidence. Furthermore, it establishes standards for comparison by which the reported visibility for any meteorological situation can be referred to the median value for the relative humidity and wind direction group, and thus the diffusion efficiency for that situation can be estimated.

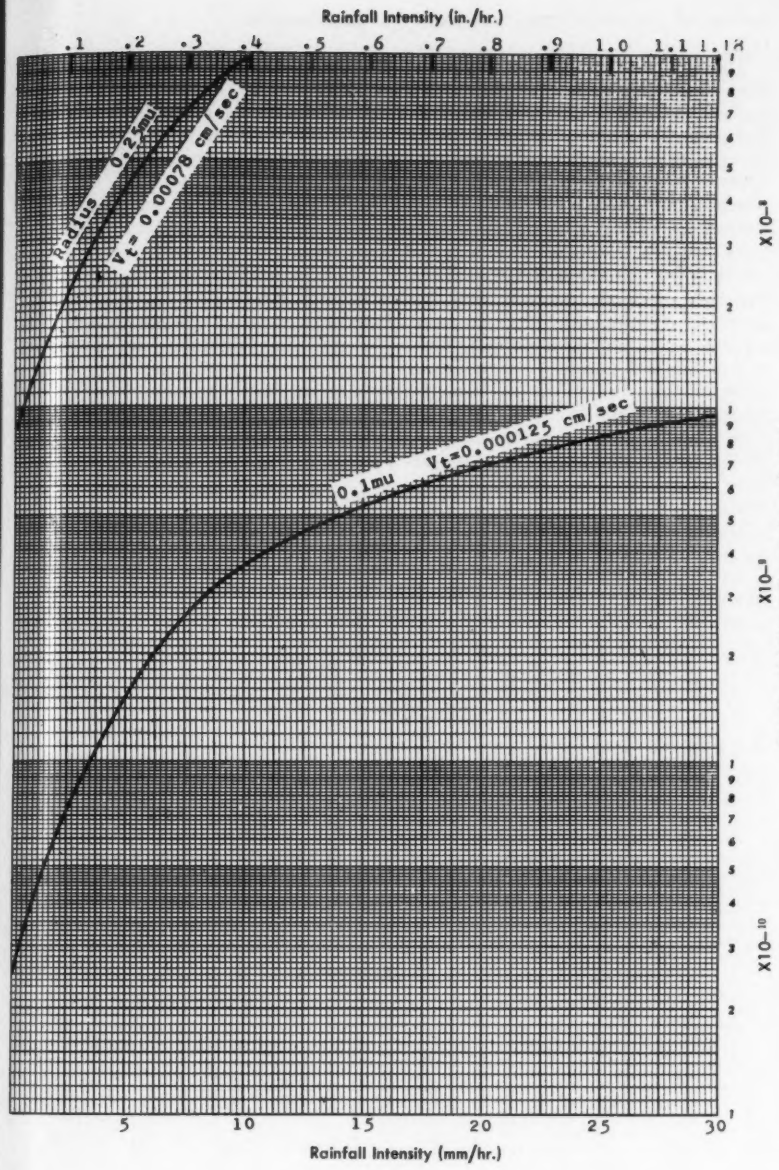


Fig. 6-c.

Once the general utility of the visibility reports has been established, an extensive series of statistical studies can be planned to utilize this information. One example is the testing of various cloud type and wind speed relationships. If the visibility data can provide a means for estimating the diffusion characteristics of the atmosphere on the basis of wind speed and cloud type alone, and if this means of estimating can be confirmed by chemical sampling and analysis, then such an estimate can be made at any time by persons relatively unskilled in meteorology. Thus, a means will be provided by which operating personnel in industrial plants will be able to utilize meteorological control of undesirable pollution in situations in which meteorological control is feasible.

d. Wind

The use of wind data from official climate compilations has always been somewhat of a problem. The exposure of the instruments, the type of instruments and, of course, the method of compilation have to be taken into consideration. But, in spite of these difficulties, much valuable information can be extracted. As examples, let us again take the Houston project. Here the "raw" hourly values for Houston and Ellington were analyzed in the following manner:

> For typical air trajectories for four selected months, a compilation was made of the hourly wind observations for each of the 24 hours. This produced a table from which could be selected the most frequent wind direction per hour and the average wind speed per hour. From this, a vectorial summation could be made and a hypothetical prevailing wind speed and direction calculated. When compared with standard U.S.W.B. statistics for prevailing direction and mean hourly speed, it was found that the August and November months differed appreciably. On close examination, it was found that local conditions—such as drainage winds and sea breeze made the hypothetical trajectory complicated to the extent that a reanalysis of "prevailing" wind is necessary.

A look at Fig. 8 shows that the November and August trajectories have potential fumigation possibilities. If we assume that the shifting of the winds amounts to a shifting of the mass of pollutants, then the reversal of wind directions evident on the hypothetical trajectories for August and November indicates a reversal of direction of pollution movement and hence an extension of the time the pollutant remains over the city.

This type of analysis points up the fact that a breakdown of prevailing winds can lead to some very informative data. Another method of analysis consists of compiling wind velocities during persistent air mass types and frontal situations, Fig. 9. From this procedure can be ascertained flow patterns during stability conditions ascribed to the various meteorological events. Hence, any count of specific events automatically infers the prevailing wind conditions.

In terms of wind flow accompanying stability parameters, compilations can be made of wind flow accompanying cloud types. In this manner, degrees of stability are assigned to cloud types and the prevalence of specific cloud types from certain directions infer a prevalence of specific stability parameters from certain directions.

e. Cloudiness

In the Standard Climatology, the cloudiness is usually fairly anonymous. In the search for pertinent data it is highly desirable to delineate the cloud types as they can be interpreted as visual stability indicators. In determining the worst possible pollution situation, we have found that a stratus type

Table VIII—Monthly Stratus Distribution as Percentages of Associated Monthly Wind Speed Categories

0–3	4–12	13–24	25+
1	48	50	1
2	40	56	2
1	50	48	1
1	46	49	4
2	44	53	1
9	68	23	0
5	55	39	1
8	85	7	0
2	72	26	0
0	59	39	2
0	43	56	1
3	53	43	1

cloud exists under conditions favorable for fumigation. Hence, a close examination of the frequency of stratus occurrence, the dominant direction of flow accompanying stratus, and the length of time a stratus deck is in existence should reveal the relative frequency of potential fumigation conditions.

The example furnished by the Houston study illustrated an interesting method of utilizing the statistical data. Examining the charts we found that though the monthly distribution of stratus by wind direction and the climatological wind roses are generally the same, and hence fumigation conditions would occur under "normal" wind conditions, it was found that late Spring, Summer, and early Fall had very few incidences of stratus. For the remaining portion of the year, it was feasible to compute a fumigation potential and delineate the areas downwind from the source that would be affected. This necessitated a count of the wind speed ranges, Table VIII, for stratus conditions as inputs into Suttons equation which incorporates wind speed as a major parameter in determining ground concentration patterns. It was then possible to plot theoretical distribution and duration of potentially fumigated areas.

Conclusions

a. Use of Standard Climatological Data

Depending on extent of local records, the standard compilations can provide a broad scale background for a meteorological investigation, such factors as type of climate—wet or dry, hot or cold, stagnant or well ventilated and cloudy or clear are generally available. If upper air soundings have been compiled, then a correspondingly larger picture can be obtained. In effect, the meteorological engineer starts with this picture and proceeds to examine the individual observations with an eye toward grouping the data to reveal information as to pollution potential.

b. Use of Observational Data

The compilation and analyzing of raw data and the conversion into usable forms is essentially the function of the meteorologist. It was shown that certain techniques can be utilized to pro-

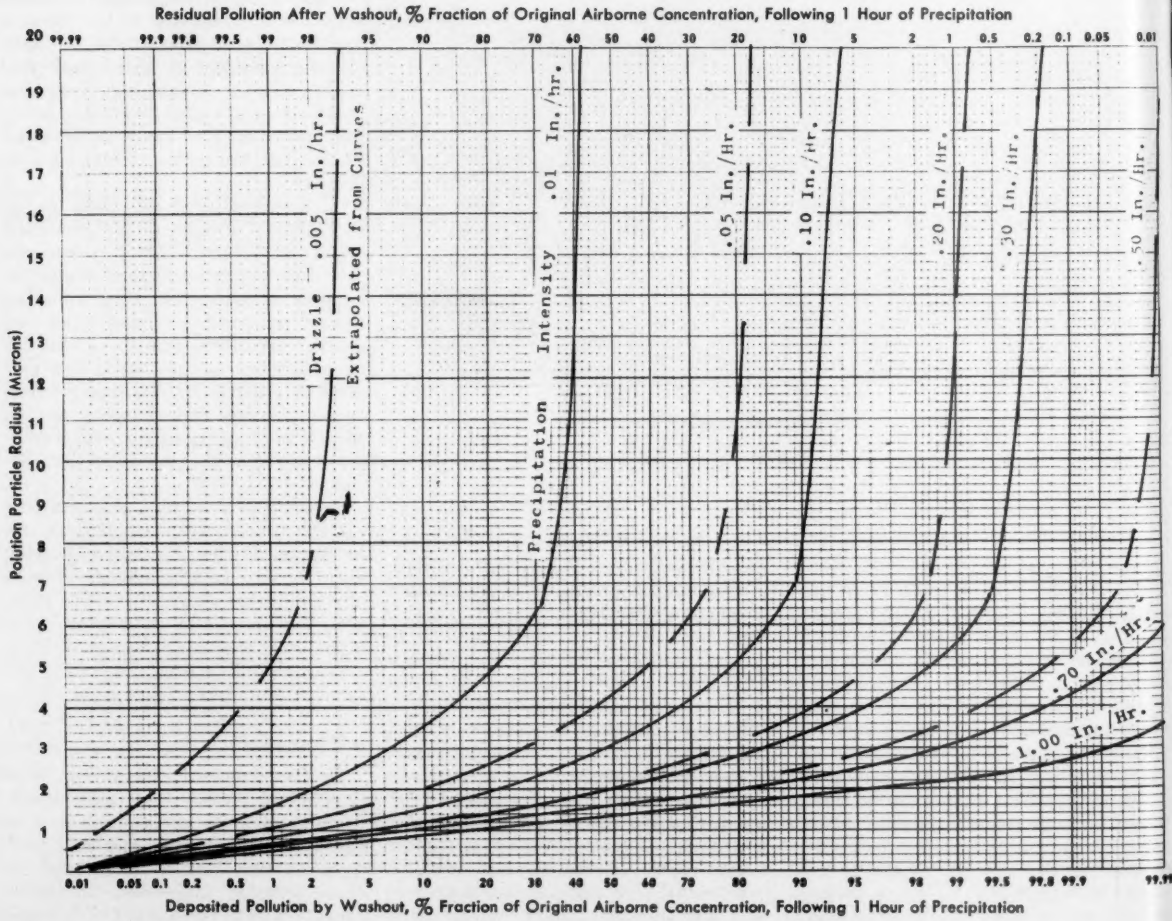


Fig. 7.

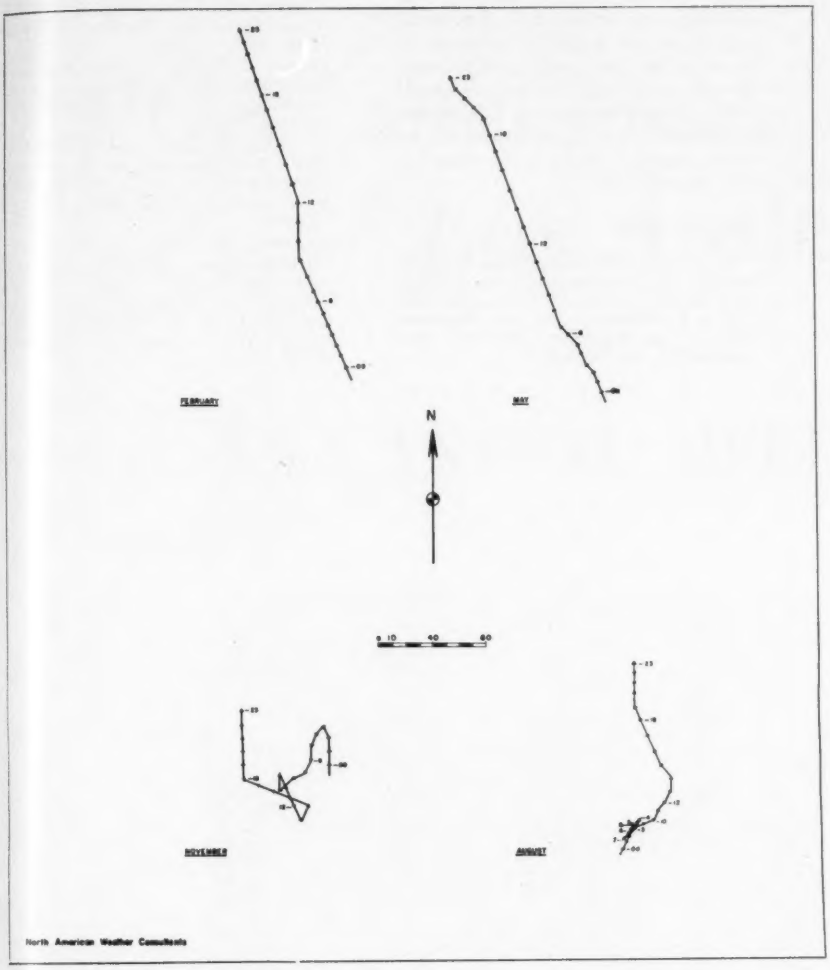


Fig. 8. Typical air parcel trajectories for selected months (Houston, Texas).

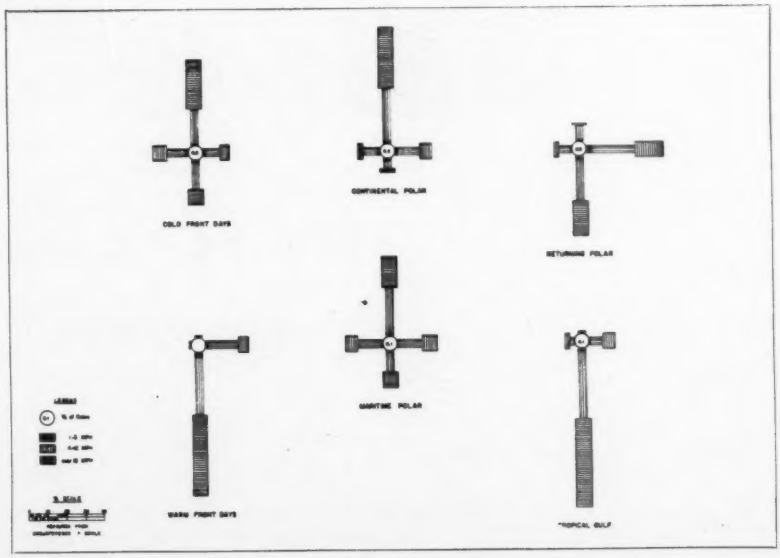


Fig. 9. Distribution of wind velocity groups by air masses December, January, February. (Houston, Texas airport.)

vide this service. Reiterating briefly the methods employed in Section 2 we have:

Temperatures—Rate of change computations.

Precipitation—Washout amounts and various ways of finding Residual Pollution.

Visibility—Combined with wind and humidity values for determination of pollution trajectories

Winds—Monthly trajectories and various combinations with other parameters.

Cloudiness—Visible stability indices.

The above certainly does not exhaust the possibilities of specialized climatology. The emphasis on precipitation, visibility, and winds is indicative of the importance to pollution problems of these parameters. It is certainly conceivable that other parameters could yield valuable information if processed according to valid hypotheses and in no other science is there more room for such hypotheses!

Acknowledgment

We are indebted to Southwest Research Institute and its Senior Chemical Engineer, Dr. Herbert C. McKee for the support in the Houston, Tex., investigation. Many of the techniques described were derived from this Project.

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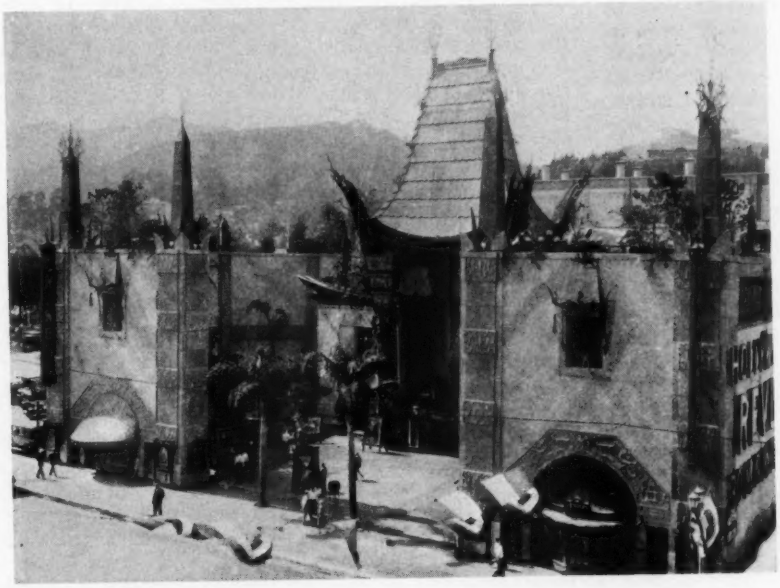

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Determining IMPACTION EFFICIENCIES *of Mist Collection Equipment**

W. E. RANZ† and **E. J. KATZ**, The Pennsylvania State University, University Park, Pennsylvania

Introduction

Impaction Efficiency

A fundamental characteristic, indeed the purpose, of a mist collector is its ability to force particles out of a gas stream and to cause them to impact upon a collecting surface. The collecting surface may be a collecting wall or body, or a liquid film on the wall or body. A measure of this ability to separate particles from the gas flow is the impaction efficiency[4] of the collector. Since particles which do not reach the collecting surface cannot possibly be separated from the gas stream as it moves through the collector, the impaction efficiency represents a maximum possible collection efficiency or over-all ability for particle removal.

Determining what a collector will not do in the way of removing small particles is a better test of performance than measuring how completely the collector will remove large particles. With this criterion in mind, the sampling system was designed to establish conditions where some but not all of the particles are removed, thereby revealing basic limitations on collector performance.

Test Equipment

The experimental work, of which an illustration is presented in this paper, was performed with equipment specifically designed for the purpose of rapidly testing inertial type mist collectors. This equipment is completely described in "A Test Method for Evaluating Mist and Dust Collection Equipment," by W. E. Ranz and E. J. Katz, Engineering Research Bulletin B-73, The Pennsylvania State University, August, 1958.

A 4000 scfm, open-circuit, air flow system is the main feature of the test equipment.[1] Fuel oil mists of several concentrations and drop sizes can be introduced into the air stream, and collectors can be inserted in a test section which is part of the airflow system.

Sampling sections before and after the collector that is being tested are 18-inch lengths of 14-inch dust. Sampling ports are provided by welding on the sides of the duct carefully aligned $^3/_4$-inch and 1-inch pipe couplings and cutting holes in the duct at these points. Ports are located at the top and bottom and on the sides of the sampling sections so that vertical or horizontal probe traverses can be obtained by sliding the sampling tube through a packing gland in a $^3/_4$-inch or 1-inch pipe plug.

Within these sampling sections velocity profiles of the gas stream, concentration profiles of the mist and the mist drop size distribution were determined.

Test Instruments and Test Equipment Characteristics

Velocity Profiles

Velocity profiles were established for the sampling sections by traversing a Meriam M-167 15-inch pitot tube across the section. This tube is equipped with a packing gland in a $^3/_4$-inch pipe plug. Impact pressures, pressure differences, and static pressures were measured via three-way stopcocks using appropriate Meriam inclined manometers.

The velocity profile is used to determine iso-kinetic sampling rates for mist concentration and size distribution tests, thereby reducing sampling errors. It is also important in establishing the existence of a developed turbulent flow entering the test collector. This permits assigning a gas velocity to the impaction process in the collector.

Concentration Profiles

The test aerosol was sampled through a 0.70-inch I.D. steel sampling tube. The front end of the tube is tapered and streamlined. A $1^3/_4$-inch radius, 90-degree bend carries the sampling tube out through a packing gland to a quick opening and closing plug valve and impactor train or filter canister as shown in Fig. 1.

Concentration measurements are made by attaching a filter canister directly to the sampling tube. A canister consists of two 6-inch sections of 4-inch tube with flanges hinged together. The flanges are faced and have $2^3/_4$-inch diameter holes. In use, one to three layers of glass-fiber filter paper and a backing screen are pressed between the flanges by a latch with a tightening screw. A seal is effected by a $3^1/_2$-inch O-ring.

Glass-fiber filter paper, which contains strands with diameter of the order of 1 μ, was chosen to avoid humidity effects in gravimetric analysis. Wherever possible, more than one paper is used so that negligible pickup on the second or third layer is an indication of complete recovery by the filter. Weighings are made on a rapid analytic balance with scale divisions of 0.0001 g.

The volumetric sampling rate is set to give an intake velocity equal to the local velocity at the place of sampling. Sampling time for concentration measurements (about five minutes), which resulted in approximately 0.1 g. of mist collected, is controlled by a plug valve.

Fig. 2 shows a concentration profile taken in the duct at the sampling section before the test collector. It supplies the desired information that the mist is well mixed and the concentration is uniform when the test aerosol enters the collector being tested.

Fig. 3 illustrates the errors introduced by line losses in side sampling and shows that correct concentration measurements cannot be obtained unless the mean and sampling velocities are relatively small (how small depends on the size of the mist particles). Dilution of the mist requires that the concentration be inversely proportional to the average air velocity. The apparent concentra-

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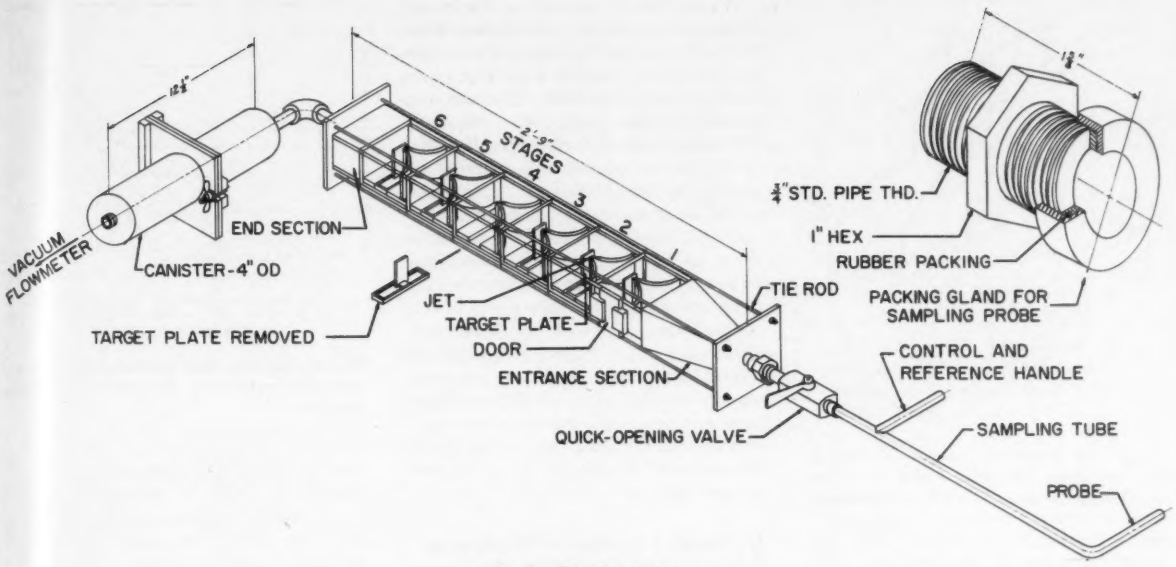


Fig. 1. Sampling train.

tions are less by an amount which can be predicted by considering impaction on the bend of the sampling tube.[4] Increasing the diameter of the sampling tube can alleviate but not eliminate this unwanted impaction of the test aerosol.

Correct measured concentrations, also shown in Fig. 3, were obtained with a submerged canister, which is illustrated in Fig. 4. The capsules inside the filter canister were packed with No. 800 Pyrex brand glass wool.

Drop Size Distribution of Test Mists

Also shown in Fig. 1 is the series impactor used to determine the drop size distribution of the test aerosol. Details of an impactor stage are shown in Fig. 5. The plate spacing ratio, i.e., the ratio of jet width to the distance from the throat to the impactor plate, is unity. Jet widths in the series are 0.266, 0.219, 0.172, 0.110, 0.062, 0.031-inch. The final stage is a filter canister, previously described. For each test the impact plates are covered with glass-fiber filter paper which absorbs the impinged mist particles.

For the test equipment and its mist generators the sampling time was varied from five to 30 minutes, depending upon conditions. For a gravimetric analysis the maximum collection for any one target plate before saturation was limited to the order of 0.2 g. Total mist collected in the series impactor and canister varied from 0.25 to 0.5 g. The data were analyzed according to the procedure outlined in Ref. 5, and Fig. 6 shows examples of apparent size distributions obtained for three different test mists at a sampling velocity of 6 fps.

It is noteworthy that size distributions obtained in this way plot nearly as straight lines on log-probability coordinates, with dispersions nearly the same as that for the original gas-atomized spray. The lines cannot be extrapolated into cumulative percentages greater than about 95 percent because maximum sizes are involved.

Although the data of Fig. 5 were taken at relatively low velocities, the total collection measured by the impactor train did not add up to known concentrations. About 10 to 20 percent of the mist, depending upon the actual sampling velocities involved and the size of the mist particles sampled, was not accounted for on the impact plates of the

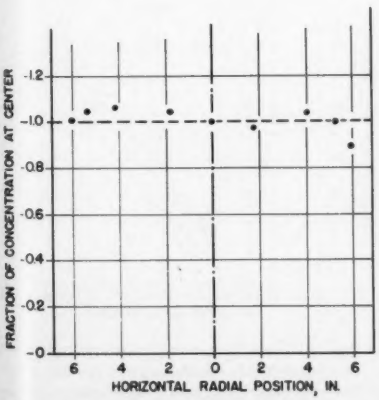


Fig. 2. Mist concentration profile in duct at sampling section before test section.

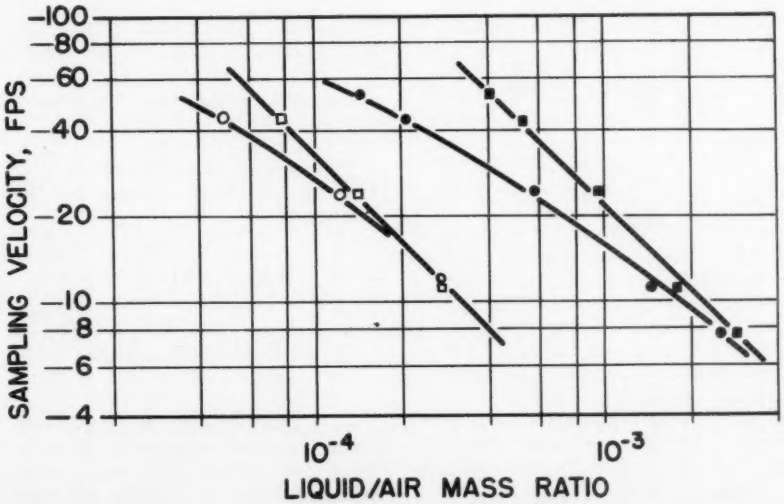


Fig. 3. Effect of sampling velocity on apparent concentration. Apparent mass median diameter approximately 6 microns. ■ Submerged canister. ● Side-sampling canister. Apparent mass median diameter approximately 3 microns. □ Submerged canister. ○ Side-sampling canister.

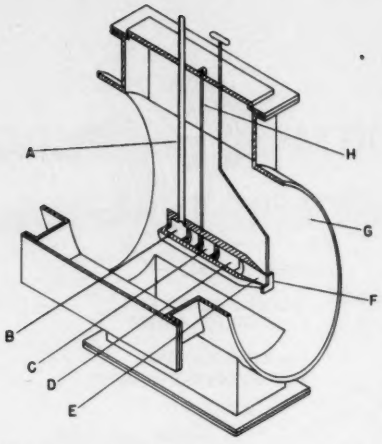
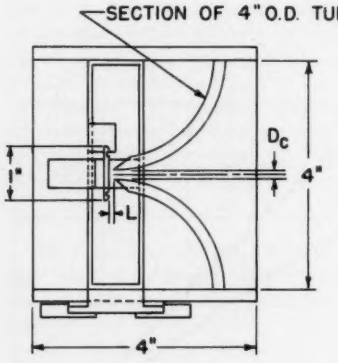


Fig. 4. Submerged filter canister. A—Vacuum line. B—Spring to hold stages in place. C—Clean-up stage $1^{7}/_{8}$"—I.D. D—Collection stage $1^{7}/_{8}$"—I.D. E—Entrance section $^{1}/_{2}$"—I.D. F—Entrance stopper for timing test. G—Special section inserted in primary duct; length 18". H—Positioning rod.

impaction stages and was collected mainly on the walls to the sides of the impact plates of the first three stages.

Fig. 7 shows the effect of sampling velocity on the apparent size distribution of a test aerosol. The differences between curves are due primarily to impaction in the sampling tube. Single data points were also obtained with an impactor stage that fitted into the submerged canister of Fig. 4. Two such points are also shown in Fig. 7. It probably represents the location of the true size distribution curve.



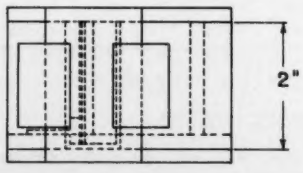


Fig. 5. Detail of impactor stage.

Because the data points in Fig. 6 and 7 depend on relative rather than absolute collection by the stages, the results, except for the largest cumulative percentages, are peculiarly insensitive to impaction bias *within* the impactor. This was demonstrated by the fact that the impactor operated in parallel reported the same mist size distribution as the impactor operated in series.

Despite errors in the size distribution curve as measured by a side-sampling impactor train, the system described has many advantages for purposes of testing the performance of mist and dust collection equipment. It gives consistent and reproducible results that are relatively easy to obtain. And, as will be shown, impactor bias need not affect an interpretation of the data with regard to the efficiency of impaction of a collector being tested.

Differential Method of Analyzing Experimental Impaction Efficiencies

Evaluating a Collector with a Prejudiced Sampling System

Since sampling through the curved sampling tube and series impactor results in an apparent mist size distribution which is smaller than the correct value throughout the range of sampling, it is necessary to consider the feasibility of using this sampling system to analyze the impaction efficiencies of mist collectors.

Consider n-drops of the test mist to lie within a particular narrow range of drop diameters. If the sampling system has a series of unwanted efficiencies, N_1, N_2, . . ., N_k, for this narrow range of drop sizes, then the number of drops of this size the sampler will report to be originally present in the stream is $n(1 - N_1)(1 - N_2)\ldots(1 - N_k)$. If the collector being tested has an impaction efficiency N_I for this same range of sizes, the number of drops removed by the collector is nN_I, leaving $n(1 - N_I)$ to reach the second sampling area. The sampler now collects $n(1 - N_I)(1 - N_1)(1 - N_2)\ldots(1 - N_k)$ droplets.

The apparent impaction efficiency of the collector, as determined by the sampler, is:

$$\frac{n(1 - N_1)(1 - N_2)\ldots(1 - N_k) - n(1 - N_I)(1 - N_1)(1 - N_2)\ldots(1 - N_k)}{n(1 - N_1)(1 - N_2)\ldots(1 - N_k)} = N_I$$

That is, the apparent impaction efficiency is the correct impaction efficiency. Thus, if the unwanted efficiencies in the sampling system are exactly the same when sampling before and after a collector being tested, it can be argued that a biased sampling system will give a correct impaction efficiency for the collector. It must be remembered, however, that the unwanted efficiencies are a function of sampling velocity, and that sampling before and after the collector must be carried out at the same sampling velocity.

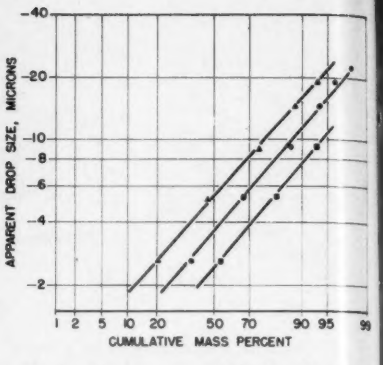


Fig. 6. Apparent size distribution of test mist. Sampling velocity—6 fps with side-sampling impactor.

Correlating Data on Collector Performance

The impaction efficiency of a mist collector is primarily a function of particle size D_p, and is usually more efficient for larger sizes. The particle size, particularly in the case of inertial separators, can be generalized in terms of a dimensionless variable N_D where

$$N_D = (\rho_p v_0/18\,\mu_g\,D_c)^{1/2}\,D_p$$

v_0 and D_c are, respectively, the characteristic velocity and the linear dimension of the collector, ρ_p is the particle density, and μ_g is the gas viscosity.

It is the purpose of the test method to determine N_I as a function of N_D, or rather N_I as a function of some average N_D over a narrow range of N_D. Such information is obtained with the series

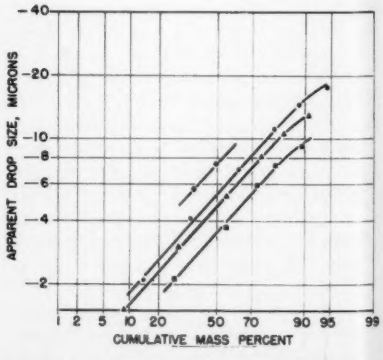


Fig. 7. Effect of sampling velocity on apparent size distribution. ◆Submerged impactor stage. Side-sampling impactor. ●Sampling velocity 10 fps. Sampling velocity 20 fps. Sampling velocity 35 fps.

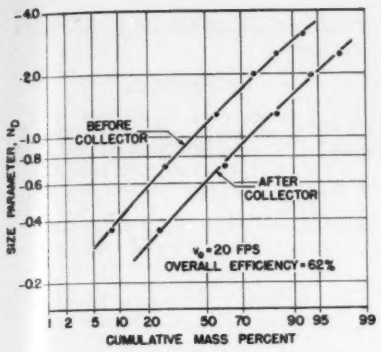


Fig. 8. An example of impactor sampling data.

impactor train by sampling the mist before and after the collector being tested.

An impact stage has the ability[2,3,5] to collect on the impact plate what amounts, in mass, to all particles above a certain characteristic size D_{pc}, where subscript c refers to the critical or cut value. Correspondingly, each stage has a characteristic N_{Dc}, which has a base value of 0.49 for a plate spacing ratio of unity. This value is modified by corrections for non-Stokes' Law behavior of particle motion.[5]

In a series impactor train, those particles which get past one stage and impact on the next have dimensionless sizes which range between

$$N_{Di} = (v_0/v_{0i})^{1/2}(D_{ci}/D_c)^{1/2}N_{Dci}$$

and

$$N_{D(i+1)} = (v_0/v_{0(i+1)})^{1/2} (D_{c(i+1)})/D_c)^{1/2}N_{Dc}(i+1)$$

with values depending primarily on accurate knowledge of velocities and dimensions both in the collector under test and in the impactor stages, and on the validity of previous work with jet and plate impaction stages.[2,3,5] Because of the additional requirement of isokinetic sampling, it should be noted that the velocity ratio becomes a ratio of flow cross sections and N_{Di} depends only on the geometry of the sampler and the collector. The values of N_{Di} are peculiarly insensitive to inaccuracies in measurements of the gas and liquid properties and other test conditions, and to changes in these properties and test conditions.

It was shown in the preceding section that timed sampling with the impactor train both before and after the collector under test would give collection on the (i + 1)-th stage, which could be interpreted as the true efficiency for the range of sizes between the i-th stage and (i + 1)-th stage. Thus, if w_{i+1} of mist is collected per unit time on the (i + 1)th impact plate when sampling before the collector under test, and w'_{i+1} is collected per unit time when sampling after the collector under test then

$$N_I = (w_i + 1 - w'_{i+1})/w_i + 1$$

for an average N_D between N_{Di} and $N_{D(i+1)}$. Such an analysis can be made directly from tabular impactor data or from faired dimensionless size distribution curves (differential method).

Impaction Efficiency of a Simple Mist Collector

To illustrate use of the test method for evaluating impaction efficiencies, Table I shows impactor sampling data taken before and after wire screening when a mat formed from several layers was tested as a mist collector. The data are presented in graphical form in Fig. 8.

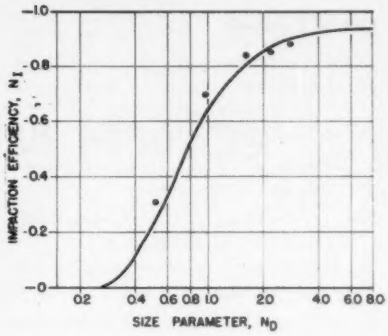


Fig. 9. Impaction efficiency of simple mist collector. ——Theory based on the impaction efficiency of an isolated cylinder. ●Difference analysis of impactor data.

Fig. 9 shows experimental values of N_I versus N_D for the same screen filter, the result of a difference analysis of the impactor data of Fig. 8. The range of partial efficiency is in good agreement with theory based on the impaction efficiency of a cylinder.[1]

Discussion of Test Method for Evaluating Impaction Efficiencies

Experience and theoretical analysis suggest that impaction efficiencies are conveniently evaluated with the foregoing test method. Reproducible and consistent results can be obtained by routine testing. Critical particle size and velocity ranges for rapidly varying efficiency can be determined. Essentially, the method compares the impaction efficiency of the collector under test with the impaction efficiency of another collector, the rectangular jet impactor.

A given set of impactor jet widths and sampling-tube sizes restricts the range of particle sizes N_D for which efficiencies N_I can be obtained. A simple way to extend the range is to vary the sampling-tube diameter. With isokinetic sampling, this results in a change in the characteristic velocities of the impactor stages. For example, increasing the sampling tube cross section and suction rate by a factor of two results in a decrease in the N_D range by a factor of $\sqrt{2}$. Although it is desirable to minimize the difference in cut sizes between stages, designs are limited by overlapping particle-size ranges.

As long as agglomeration and reentrainment do not occur in the collector under test, and as long as the impactor can inertially collect the mist sampled after the collector under test (electrostatic precipitators have not been studied), this test method for evaluating impaction efficiency as a function of particle size appears to have wide application.

Table I—An Example of Impactor Sampling Data

Stage No.	Size Parameter, N_D	Collected Before, g/10 min	Cumulative Passing Stage (Before), %	Collected After, g/10 min	Cumulative Passing Stage (After)[a], %	N_I for Mist Passing Previous Stage	Geometric Average N_D Between Previous Stage and Stage
1	3.1	0.0433	92.6	0.0080	—	—	—
2	2.5	0.0443	85	0.0053	97.5	0.88	2.8
3	2.0	0.0542	76	0.0081	94	0.85	2.2
4	1.28	0 1070	57	0.0170	86	0.84	1.60
5	0.72	0.1723	28	0.0523	61	0.70	0.96
6	0.36	0.1109	8.7	0.0771	25	0.31	0.51
Canister	—	0.0509	—	0.0524	—	—	—

Data	Collector Tested
Sampling rate at center of test section, 22 fps v_0, 20. Air temperature, 90° F. Air pressure, 22.0 in. Hg. $N\rho_g = 24$; $N_{Dc} = 0.49 \times 1.07 = 0.52$.	Screen filter composed of 4 layers of 14 x 18 strands/in., 0.01035 -in. diameter wire, sandwiched between 5 layers of 2 x 2 strands/in., 0.563-in. diameter wire.

[a] First stage collects re-entrained mist and collection is not included in cumulative percent calculation.

List of Symbols

D_c = characteristic linear dimension of collector; width of rectangular jet in jet impactor stage

D_p = diameter of mist particle

L = distance of plate from jet outlet in jet impactor stage

N_D $(\rho_p v_0/18\,\mu_g D_c)^{1/2} D_p$ = particle size and velocity parameter

N_I - L/D_c = plate spacing ratio of impactor stage

$N\rho_g$ $9\,\rho_g v_0 D_c/\rho_p \mu_g$ = parameter accounting for gas inertia effects during those times, and under those conditions, where Stokes' Resistance Law does not apply to the motion of the particle

v_0 = characteristic gas velocity in collector; velocity of jet in jet impactor stage

μ_g = gas viscosity

ρ_g = gas density

ρ_p = density of liquid in mist particles

Subscript "i" refers to an impactor stage.

Other symbols are defined at their point of use.

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Auto Exhaust: COMPOSITION and PHOTOLYSIS PRODUCTS*

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Automobile exhaust is becoming widely recognized as one of the major sources of air pollution. Although each car makes only a minor contribution, the combined exhausts from the millions of cars present in a modern large city add up to a staggering total of pollutants emitted to the atmosphere. To assess this source of pollution, and preliminary to the study of methods of reducing it, a complete and reliable analysis of the exhaust under the various modes of engine operation is required. A number of papers on this subject appeared in a recent issue of the *Journal of the Air Pollution Control Association*. One of these papers[1] describes the application of infrared absorption spectroscopy to this problem. In this work samples were drawn from the exhaust pipe through Drierite into a one-meter infrared absorption cell. The spectrum from 2.5 to 6.5 μ was scanned revealing bands of carbon dioxide, carbon monoxide, water, nitrogen dioxide, and hydrocarbon (CH).

In the present paper some simple analyses of engine exhaust using a long-path infrared absorption cell are described. Some of these samples, diluted with oxygen, were irradiated with a mercury vapor lamp which simulates sunlight. The products of the photochemical reactions were determined and are also reported. This was done to provide information on the products to be expected when the exhaust is vented to the atmosphere and allowed to react under the influence of sunlight.

Samples Were Taken on the Road

The test car was a six-cylinder, 1955 Chevrolet with standard transmission. When the accelerating, decelerating, and idling samples were taken the mileage was 2,000 and it was burning a mixture of two regular gasolines. When the cruising sample was taken several months later the car had a mileage of 3500 and was burning another regular gasoline.

"Grab samples" of exhaust were taken with the car on the road. The following technique was used: A five-liter Pyrex flask was evacuated in the laboratory and about eight feet of Tygon tubing was attached to it through a stopcock. The evacuated flask was held in the back seat and the tube was passed through the window and pushed about a foot and a half into the exhaust pipe. With the car in operation the stopcock was opened at the appropriate moment to allow the sample to be sucked into the flask. The flask was filled in three or four seconds. The accelerating sample was taken in second gear, the cruising sample at 30 mph in high gear, the decelerating sample at about 25 mph in high gear with the foot off the gas pedal, and the idling sample in a parking lot.

The exhaust gases were sampled directly; they were not passed through any drying agents or other absorbents. They were, however, mixed with oxygen before analysis to oxidize any nitric oxide to nitrogen dioxide which is more easily detected spectroscopically.

Spectra Recorded with a 120 Meter Path

Infrared analyses and photolysis experiments were carried out with the long-path infrared cell which has been described previously.[2,3] This cell is currently being used with a Perkin Elmer double-pass monochromator and a Nernst glower light source. For these analyses a sodium chloride prism was used and the cell was set at a path length of 120 meters. The grab samples contained in the five-liter flasks were transferred to the cell by the following technique: the sample was first expanded to a total volume of about eight liters and brought to atmospheric pressure with pure oxygen. It was then allowed to stand for a few minutes to oxidize the nitric oxide to nitrogen dioxide. The flasks were then attached to the pre-evacuated cell and the stopcock opened to allow the sample to expand into the cell; the pressure in the sampling flask of course fell to a very low value. Next the sample flask was filled with oxygen and this gas again expanded into the cell to flush the remainder of the exhaust gas from the flask into the cell. The pressure in the cell was then raised to one atmosphere with pure oxygen and the spectrum from two to 15 μ was run. A blank spectrum was obtained by preparing a sample of oyxgen to contain, as nearly as possible, the same amount of water vapor as the exhaust sample. Thus the spectra as plotted do not show the true water vapor content of the exhaust. The nitric oxide content of a sample of accelerating exhaust was measured using a lithium fluoride prism. This exhaust sample was collected directly in a one-meter absorption cell and was not mixed with oxygen. The higher dispersion provided by this prism made it possible to detect the weak nitric oxide lines in the vicinity of 5.5 μ in spite of the overlapping water vapor absorption.

Several points should be noted concerning the method of sampling used here. First, since no drying agents are used and the sample is expanded into the cell the chances of losing any components of the exhaust are minimized. Since five liters of exhaust were expanded into a cell of 500 liters volume the dilution was 100 fold. Thus similar results could have been obtained by sampling directly into a one-meter cell.

Four Modes of Operation Were Sampled

Infrared absorption spectra (are shown in Figs. 1 and 2) of the exhaust gases from the four modes of engine operation: acceleration, deceleration, idle, and cruise. Concentration of the various components of the exhaust gas are shown in Table I. In a general way these results are consistent with those reported by earlier workers. In particular the amount of nitrogen dioxide was found to be much larger during acceleration than during any other phase of

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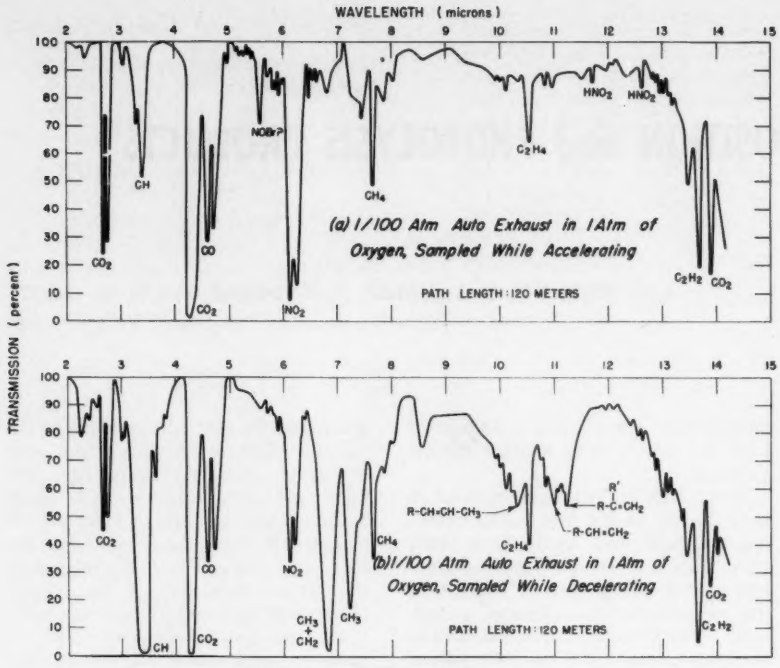
WAVELENGTH (microns)
TRANSMISSION (percent)
(a) 1/100 Atm Auto Exhaust in 1 Atm of Oxygen, Sampled While Accelerating
PATH LENGTH: 120 METERS
(b) 1/100 Atm Auto Exhaust in 1 Atm of Oxygen, Sampled While Decelerating
PATH LENGTH: 120 METERS

Fig. 1. Infrared spectra of exhaust gases.

engine operation. The total hydrocarbon as indicated by the CH band at 3.4 μ and by the olefin bands at 10 to 12 μ is greatest during deceleration. A number of compounds are conspicuous by their absence. Particularly striking is the lack of any carbonyl compound absorption at 5.75 μ. This fact and the absence of absorption near 3.6–3.7 μ indicates that little, if any, aldehyde is present. The infrared spectra of exhaust gases shown in the paper previously cited[1] show neither aldehyde nor carbonyl absorption.

In this earlier work it might have been suspected that the carbonyl compounds were removed by the agents used to dry the gases. This cannot be true in the present case because no drying agents were used and so it must be concluded that little, if any, carbonyl compounds are present in the exhaust gas.

The sample of exhaust gas taken during acceleration and to a lesser extent the sample taken during cruising show nitrous acid in addition to nitrogen dioxide. This acid exists in the gas phase in equilibrium with nitrogen dioxide, nitric oxide, and water:[5,6]

$$NO_2 + NO + H_2O \rightleftharpoons 2HNO_2$$

This sample, therefore, contained a considerable amount of nitric oxide which was not oxidized by the dilution with oxygen. A separate sample of exhaust gas from the accelerating phase was expanded directly into the one-meter gas cell and the five to six μ region of the infrared spectrum examined using a lithium fluoride prism. The nitric oxide concentration was found to be about 800 ppm.

Concentrations Are Dependent on Mode of Operation

Examination of Table I reveals that the compounds detected fall into several distinct classes. Olefins (except ethylene) and total hydrocarbon are present in 10 times greater concentration during deceleration than during any other phase of operation. This is probably caused by a higher concentration of unburned hydrocarbons pumped through the engine when manifold vacuum becomes high. The methane, ethylene, and acetylene are roughly the same in all phases of engine operation being only a little higher during deceleration than the other phases. These are probably products of cracking and partial oxidation of the fuel. Carbon monoxide follows a similar pattern except that its concentration is quite low during cruising when combustion is most complete. Carbon dioxide concentration is about six percent except during deceleration when it falls to about one-half this value, probably due to failure of the fuel charge to burn. The nitrogen dioxide concentration follows quite a different pattern. It is very low during idling and very high during acceleration. This difference is probably even more marked than the values given in Table I would indicate because the nitrogen dioxide probably represents only a portion of the total oxidized nitrogen in the sample. The very high value is apparently caused by the freezing of the NO by the rapid expansion stroke. When the car is in second gear (as it was when the accelerating sample was taken) this expansion occurs more rapidly, for a given car speed, than it does in high gear. Thus the gas is cooled more rapidly and the unstable oxides have less chance to decompose

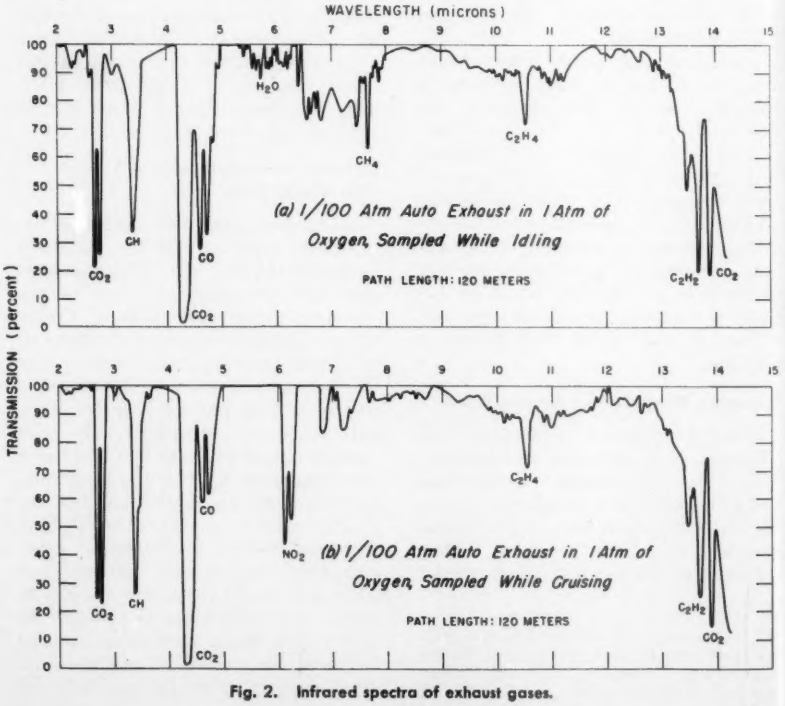
WAVELENGTH (microns)
TRANSMISSION (percent)
(a) 1/100 Atm Auto Exhaust in 1 Atm of Oxygen, Sampled While Idling
PATH LENGTH: 120 METERS
(b) 1/100 Atm Auto Exhaust in 1 Atm of Oxygen, Sampled While Cruising
PATH LENGTH: 120 METERS

Fig. 2. Infrared spectra of exhaust gases.

Table 1—Composition of Auto Exhaust

(Concentration in Parts per Million for the Indicated Components in the Various Phases of Vehicle Operation)

Component	Idling	Accelerating	Cruising	Decelerating
Nitrogen[a] Dioxide	20 ± 10	1000 ± 100	310 ± 30	430 ± 50
Carbon monoxide	20,000 ± 1000	20,000 ± 1000	8800 ± 400	18,000 ± 1000
Methane	3400 ± 300	5100 ± 500	430[b]	6100 ± 600
Ethylene	400 ± 50	500 ± 50	400 ± 50	800 ± 100
Acetylene	330 ± 50	330 ± 50	280 ± 40	620 ± 100
1-olefins (calc. as propylene excluding ethylene)	75 ± 25	40 ± 20	75 ± 25	850 ± 100
2-substituted 1-olefins (calc. as isobutylene)	40 ± 20	10 ± 10	10 ± 10	300 ± 50
2-olefins (calc. as trans-2-butene)	10 ± 10	10 ± 10	10 ± 10	800 ± 100
Total hydrocarbons (calc. as butane, excluding methane ethylene, acetylene)	800 ± 50	470 ± 30	1030 ± 50	17,000 ± 1000
Carbon dioxide	64,000 ± 3000	59,000 ± 3000	64,000 ± 3000	33,000 ± 1500
Formaldehyde	None	None	None	None
Formic acid	None	None	None	None
Other carbonyl compounds	None	None	None	None

[a] Much of the NO_2 reported here was present in the exhaust as NO and was oxidized to NO_2 when diluted.

[b] This value may be low. The oxygen used to dilute the sample contains methane which may not have been properly allowed for in this sample.

than they do at a slower engine speed.

In the spectrum of exhaust from the accelerating phase there is a band at 5.57 μ which may be due to NOBr. Burns and Bernstein[7] have reported that NOBr absorbs at this wave length. This compound could arise from the reaction of nitric oxide with bromine present in the antiknock fluid.

Ozone and Peracyl Nitrite Are Formed When Exhaust Is Photolyzed

The sample of cruising exhaust whose spectrum is shown in Fig. 2 was irradiated for about two hours with the high pressure mercury arc. Since the original sample was diluted 100-fold the initial composition of the irradiated mixture may be obtained by dividing the concentrations given in Table I by 100. The spectrum of the products is shown in Fig. 3. The products observed are quite similar to the products found when pure hydrocarbons were irradiated with nitrogen dioxide in oxygen. Ozone was formed quickly as shown by the dotted line in Fig. 3 which represents about three ppm. Bands of compound X, now believed to be peracyl nitrite, are also prominent in this spectrum. The formation, structure, and importance of this compound are discussed at some length in recent papers.[3,4] Its concentration is estimated to be three ppm.

Other products were formic acid, alkyl nitrate, and a small amount of aldehyde. The nitrogen dioxide was completely gone at the end of about 1¼ hours' irradiation. The olefin concentrations were much reduced during this time. The concentration of carbon monoxide was unchanged by the irradiation within the experimental error of several percent. The acetylene concentration also was unaffected by the irradiation.

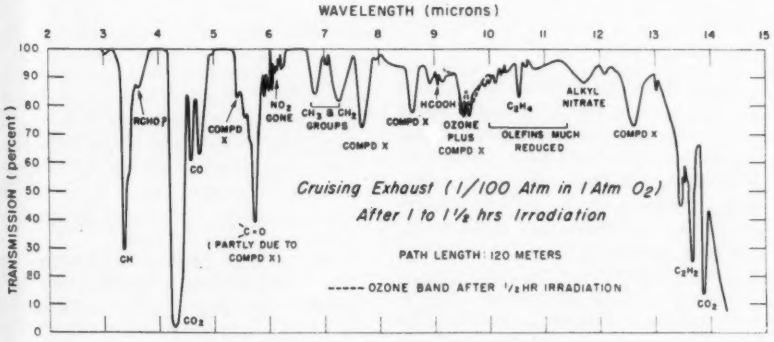

Fig. 3. Infrared spectrum of photolysis products.

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Improved TITRILOG *Sensitivity*

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Within recent years the "Titrilog"[1] was developed as a continuous recorder of concentrations of oxidizable sulfur compounds such as hydrogen sulfide, sulfur dioxide, etc., in gas streams or atmospheres. It is an automatic titrating instrument in which sulfur compounds are measured by their titration with bromine. The bromine is electrolytically generated in a solution in which the sulfur compounds are absorbed from the sample gas stream. The titration cell in which the oxidation-reduction reaction occurs forms a part of an electronic feedback amplifying system which controls the bromine generating current so that the net rate of bromine generation is at all times equivalent to the rate of absorption of the sulfur compounds. A recording milliammeter records the generating current. The net current which is over and above that required to maintain the bromine concentration at a preset "zero" level is proportional to the sulfur compound concentration in the incoming gas stream.

The Titrilog range for measurement of an oxidizable sulfur compound such as sulfur dioxide in air is specified as 0.1 to 270 parts per million (ppm) by volume. In a number of instances of interest as in the measurement of background levels of sulfur dioxide concentration normally present in a community atmosphere,[2] the measurements are in a range below the specified lower limit of the instrument. Improvement of the Titrilog sensitivity will permit such measurements to be made.

Modification

The Titrilog normally has an indicating milliammeter (A) and an Esterline-Angus milliampere recorder (E-A) to show the value of the generating current calibrated in terms of the gas under analysis. These components are shown in terms of their internal resistances in the basic schematic circuit (Fig. 1a). The indicating milliameter and the recorder have a full-scale range of one milliampere. The smallest value readable with fair accuracy is 0.01 milliamp. This corresponds to a calibrated measurement of 0.1 ppm of sulfur dioxide.

The improvement in the Titrilog's sensitivity was effected by the measurement of the generating current as a voltage drop across a known fixed resistance (Fig. 1b *see next page*). A Bristol recording potentiometer was used to measure the voltage drop across either resistance, R_A or R_E, using switch, S_2. This recorder had an expandable full-scale range from 0–1 to 0–50 millivolts. It also had zero suppression from −50 to +50 mv. Full scale consisted of 100 divisions on the chart paper. In the range of maximum sensitivity, each division was equivalent to 0.01 mv. The measured width (approximately 2.5 mm) of the divisions on the mv. recorder was about the same as that on the ma. recorder.

Improved Sensitivity

The improved sensitivity is obtained in the following manner. For a given sample of gas, the generating current arrives at some particular value which is designated as I ma. Since the deflection sensitivity of the milliampere recorder is 50 divisions per milliampere, the total deflection for a given current is 50 I divisions. For the same current of I ma, the voltage drop across a known fixed resistance, R ohms, is RI mv. The deflection sensitivity of the millivolt recorder, however, is 100/S divisions per millivolt, where S is the full-scale range in mv. The total deflection corresponding to a generating current of I ma is 100/S RI divisions. Consequently, the gain in sensitivity, G, being defined as the ratio of mv deflection to ma deflection, becomes

$$G = \frac{100\ RI}{50\ SI} = 2\frac{R}{S}$$

From this equation it can be seen that the sensitivity gain is directly a function of the resistance across which the voltage is measured and inversely related to the full-scale range of the mv recorder. In the mv recorder used, S was a minimum at 1 mv while circuit parameters limited R to about 1300 ohms. These values set the maximum potential gain at 2600.

Experimental Performance

An experimental determination of sensitivity in the measurement of sulfur dioxide was made using the 68 ohm resistance, R_A of the indicating milliammeter. Further investigations using resistance R_E of the Esterline-Angus recorder were made but at this high level of sensitivity the noise became prohibitive. Sulfur dioxide was sampled from a gas dilution system[3] which was separately calibrated for various levels of concentration by a colorimetric technique.[4] The sensitivity was determined for the most sensitive range (0–1 mv) of the potentiometric recorder. The recorder gain was adjusted to minimize the noise level without too great a loss in the recording of the input signal. The ratio of recorded to input signal was 0.86. The signal deflection upon which was superimposed noise fluctuations was taken as the deflection value from the zero base line. The noise consisted of deflections of as much as seven divisions above and below the estimated signal reading.

The results plotted on double log paper (Fig. 2) give a straight line relationship for sulfur dioxide concentration as a function of recorder deflection. The improved sensitivity is shown in the greater deflection, more than a factor of 10, of the potentiometer recorder compared to the current recorder for a given concentration of sulfur dioxide. At higher recorder ranges, the sensitivity is reduced with the advantage of less noise background.

Noise

The increased sensitivity accentuated the background noise level which initially was barely discernible. This limited the maximum gain which would otherwise be available. The maximum

* Deceased.

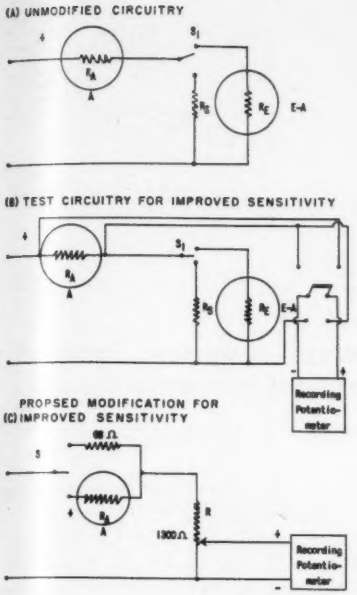

Fig. 1. Titrilog circuitry for measuring generating current.

gain permissible was that at which a small signal deflection can be separated from the background noise and still represent a low level of detection. This gain gave a signal to noise ratio of 1.5 to 2.

The zero level adjustment, a multiturn potentiometer, contributed appreciable noise at some of its settings. The voltage generating effect of the galvanometric movement in the indicating meter and the Esterline-Angus recorder also appeared to add to the noise level. In addition to the electronic tubes and the sensor electrodes, there are the electrolytic condenser shunting the meter circuit, the diode, and the choppers which may be sources of noise and are being investigated for noise properties.

Zero Drift and Suppression

The zero adjustment on the Titrilog allows the generating current to be set at any desired level. The recommended setting is in the range of 0.10 to 0.20 ma. This determines the base line from which readings are made and correlated to sampled gas concentrations. It also allows for negative or positive drift.

When the Titrilog was modified to increase its sensitivity, it was necessary to reduce the large voltage drop resulting from the zero current setting. The generating current was reduced to a minimum of 0.20 ma. This allowed for negative drift without reversing polarity. The resulting zero level setting on the mv recorder was made adjustable by the use of a zero suppression which had a range of −50 to +50 mv.

With increased sensitivity, the zero drift of the generating current became very apparent. For short periods of analyses (1–2 days duration) there was no difficulty. For monitoring purposes where it may be necessary to leave the instrument unattended for periods of three days or more, it would be necessary to arrange for automatic adjustment of the generating current. Plans are currently under way for the development of an accessory circuit to be used in conjunction with the improved sensitivity circuit and to allow for an automatic resetting of the generating current at a fixed value concurrent with the hourly zeroing cycle. Results of this work will be reported in a future publication.

Proposed Modification

Figure 1c shows the modification proposed for improved sensitivity as a result of this investigation. Initially, the sensitivity was varied by using a recorder of expandable range across a fixed resistance either R_A, R_S, or R_E. Here this effect is realized by using a single range recorder across an adjustable multiturn resistor, R. The indicating meter, A, is in the circuit only as a means of quickly adjusting for zero current level. At other times it is cut out by the switch, S, which replaces it with an equivalent resistance.

The employment of an adjustable multiturn resistor, R, used as a voltage divider and across which a less sensitive mv recorder is connected, provides a relatively inexpensive means of obtaining an expandable range of sensitivity. As an example, the resistance R (Fig. 1c) may be set at 680 ohms for a 10 mv recorder. This arrangement will provide the same sensitivity as that of a 1 mv recorder across 68 ohms (Fig. 1b).

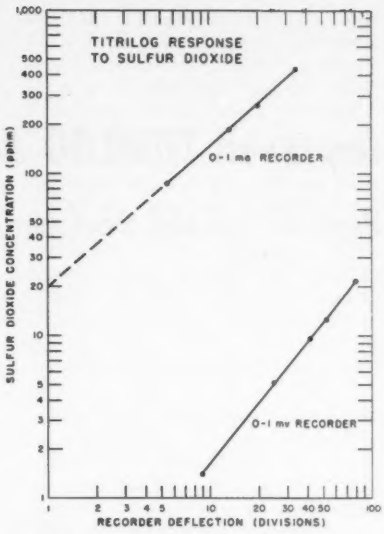

Fig. 2. Titrilog response to sulfur dioxide.

Summary

The Titrilog, as a result of recommended modifications, had its sensitivity improved by a factor of more than 10. The sensitivity was shown to have a potential improvement factor of more than 2000 if the background noise level were reduced to an insignificant level. Probable sources of noise were noted, indicating that their effects may be minimized by a selective choice of critical electronic components.

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Improved TITRILOG *Sensitivity*

Part II. Field Performance and Evaluation

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The first portion of this paper (Part I. Proposed Modification and Results) outlined the theoretical basis for increasing the sensitivity of the Titrilog by a factor of ten. This portion of the paper tells how the modification was accomplished in an instrument for actual field use, and summarizes the results of several months' operating experience.

The instrument was used in an air pollution survey being conducted in the Houston, Texas, area to obtain data on the nature and extent of air pollution problems in the area. Early in the survey, it became evident that sulfur dioxide was the best single indicator of over-all pollution levels since it is emitted by many different oil refineries, sulfuric acid plants, and other industries in the area. Therefore, it was felt desirable to obtain continuous records of sulfur dioxide concentration to determine the manner in which concentration varied, and to indicate the severity of pollution in different sections of the metropolitan area.

Extensive sampling with a mobile laboratory indicated that sulfur dioxide concentrations in excess of 0.5 ppm were occasionally found in a few localized areas. However, in the areas where continuous records were desired to indicate the hourly and daily variations, the concentration seldom exceeded 0.02 to 0.03 ppm. This meant that any of the conventional instruments for continuously recording sulfur dioxide would register zero most of the time, and it would be impossible to use such records to determine daily variations or differences in the average pollution level in different sections of the community. In view of this difficulty, the increased sensitivity appeared to be an extremely desirable feature.

Most analytical methods based on a physical or chemical measurement are occasionally subject to interferences from other impurities present. In the case of the Titrilog, other sulfur compounds in addition to sulfur dioxide would affect the instrument, increasing the indicated concentration with an instrument calibrated for sulfur dioxide. Analytical results obtained with the mobile laboratory indicated that hydrogen sulfide was found in some sections of the community at some times, but the concentrations were usually much lower than sulfur dioxide concentrations. Therefore, only very minor errors would be caused by expressing the results in terms of sulfur dioxide.

With these considerations in mind, it was decided to use a modified Titrilog, even though the work reported in the first section of this paper had not been completed when this decision was made.

General Discussion

In a private communication from J. S. Nader of the Public Health Service, it was learned that the Titrilog's sensitivity could be increased by a factor of 10 by using a more sensitive recorder. The Titrilog normally uses a 0 to 1 ma Esterline Angus Recorder to record the value of the generating current, and an indicating 0 to 1 ma meter to measure the current. Their success with a Bristol recording potentiometer led us to pursue a similar modification.

The output circuit for the Titrilog is shown in Fig. 1, with the controls set for a measurement. The resistance of the recorder plus the meter normally used is approximately 1500 ohms. At a current of 1 ma, the voltage at the recorder terminals of Fig. 1 would be 1.5 v. If a 10 to 1 sensitivity improvement in sensitivity were to be made, the recorder should give a full scale reading for 0.15 v or 0.1 ma.

A recording potentiometer measures voltage instead of current and has a high input resistance. Therefore, a resistance, R-1, of 1500 ohms will need to be placed across the recorder terminals, as shown in Fig. 2, to permit the flow of the correct generating current and to convert the current into a voltage for the recorder. The resistor should have a movable tap, see Fig. 2, so that the proper voltage can be fed to the recorder. As stated previously, for an improvement of 10 to 1, the recorder should give full scale reading for 0.15 v or 150 mv. With a recorder having this range, the tap would be at the top so the full resistance is used. If the recorder had a full-scale range of 100 mv, the tap should be at 1000 ohms or $^2/_3$ of the total. For a recorder of 10 mv full scale, the tap should be set at 100 ohms, etc.

Noise and drift are both a problem with the increased sensitivity. If the maximum noise and drift, in the original system, is equal to the smallest reading of 0.01 ma, the noise voltage across the 1500 ohm resistor will be 0.015 v or 15 mv. The signal to noise ratio would therefore be only 10 to 1. If the recorder had 100 divisions, the noise would cover 10 divisions. The bandwidth of the output circuit, Fig. 1, is approximately 1000 cycles. Therefore, to reduce the noise, the bandwidth should be reduced. Since the signal to noise ratio varies inversely as the square root of the bandwidth, for an improvement of 10 to 1 in noise, the bandwidth must be reduced by 100 or to 10 cycles. However, since a 60-cycle chopper is used, the noise fed to the output circuit will all be below 30 cps. Therefore, to reduce the noise by 10 to 1, the bandwidth must be reduced to 3 cps. The bandwidth reduction with its associated noise reduction can be accomplished with the simple RC, low-pass filter shown in Fig. 2.

For proper operation of the Titrilog, the zero adjustment must be set so that a generating current of approximately 0.1 ma flows with pure air. At the increased sensitivity, this means a voltage of 150 mv across the recorder terminals. Some means must be used to buck-out this voltage so that the recorder will

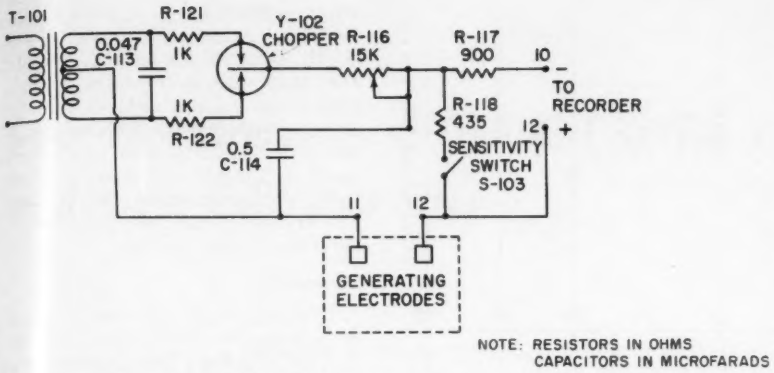

Fig. 1. Output circuit for the Titrilog with the controls set for a measurement. (From Titrilog Instruction Manual)

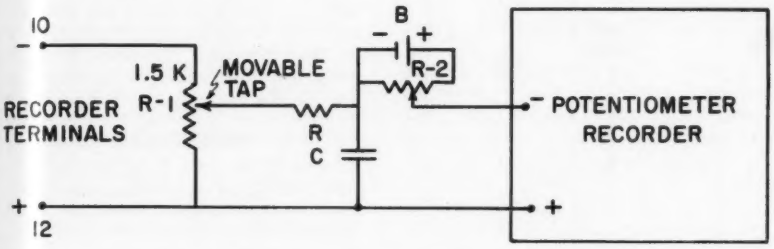

Fig. 2. Circuit for the addition of a potentiometer recorder.

not always read full scale with no input. The bucking voltage can be supplied by the battery (B) and a potentiometer (R-2) combination shown in Fig. 2. This combination, using a 1.5-v battery, will permit bucking of up to 1.5 v. If the recorder used has sufficient zero suppression in it, it can be used to correct for this condition.

The zero setting may drift with this increased sensitivity, and the noise generated during rotation of the control may make it difficult to zero. The zero adjust control (R-103) may be very touchy at the higher sensitivity and it may be necessary to add a small variable resistor in series with it for a fine control.

Modification Used

The modification used is shown in Fig. 3. A Varian Model G-11 recorder was chosen because of its low price and availability. It had an adjustable full-scale range of 10 mv to 100 mv, and was adjusted to have a range of 100 mv. With this adjustment, the recorder had a sensitivity of one chart division per 1 mv.

A Helipot was chosen for R-1 of Fig. 2. However, a 1500 ohm unit was not readily available, so a 2000 ohm unit was used and resistor R-116 (Fig. 1) was adjusted so the total resistance in the generating electrode circuit was the correct value. The tap was set at approximately half value or 1000 ohms.

The Varian recorder did not have a sufficiently wide zero-suppression adjustment and therefore it had to be augmented with the bucking system. A 1.3-v mercury cell was used for stability.

The bandwidth was reduced to less than 0.1 cycle with the filter. This reduced the noise so that it was less than one division. Without the filter, the maximum noise was 20 divisions. Drift was a problem but, by adjusting the zero-suppression so that on pure air the reading was 20 to 30 (chart scale of 0 to 100), the zero point seldom drifted to the lower end of the scale. It was necessary to use a balanced filter to reduce the noise caused by the grounded (through a large capacitor) negative terminal of the recorder.

The use of this large filter is a "brute force" method of reducing the noise. The circuit components which could contribute noise were checked and found within the specified tolerances. It was therefore apparent that any significant reduction in noise would require a complete redesign of the complete electronic system. Time did not permit this redesign and, therefore, the "brute force" filter was used.

The Titrilog was calibrated by passing air containing a known concentration of sulfur dioxide through the unit, from a polyethylene bag which served as a gas holder. Concentration of the air used for calibration was determined by a colorimetric technique.[1] The Titrilog was calibrated for a recorder deflection of 1 scale division per 0.01 ppm sulfur dioxide. This meant that, with the zero set at 25 on the recorder scale, full scale deflection corresponded to 0.75 ppm.

In actual operation, drift of the zero point was the most serious difficulty. A small electric heater, controlled by a thermostat, was installed inside the case in the hope that zero drift could be reduced by reducing temperature variations, but this was only partly successful. During some periods, the zero point would drift off the lower end of the scale. This apparently caused no damage, and the instrument resumed normal operation when the zero point moved back onto the scale; the only difficulty was that no record was obtained during the period when the pointer was off scale. Since the zero point does drift, the instrument was set to record a zero reading once an hour.

Fig. 4 shows a typical record obtained at a concentration of 0.01 ppm sulfur dioxide. This record was obtained in the laboratory, but is similar to many records obtained in actual field operation. It can be seen that the noise level is sufficiently low that a concentration of 0.01 can be distinguished readily from the zero reading. Due to the drift

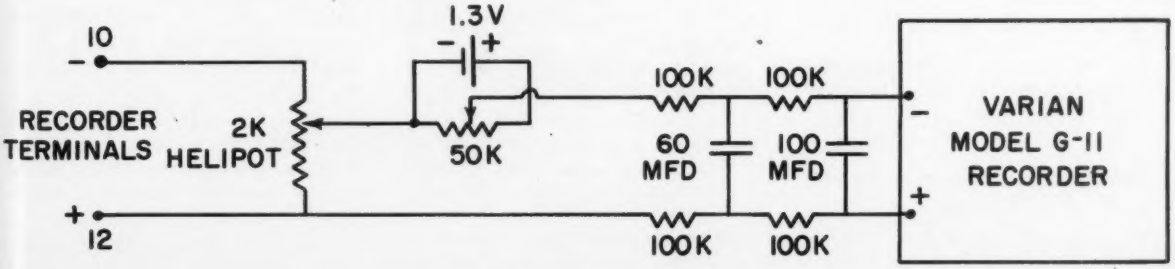

Fig. 3. Titrilog recorder modification used.

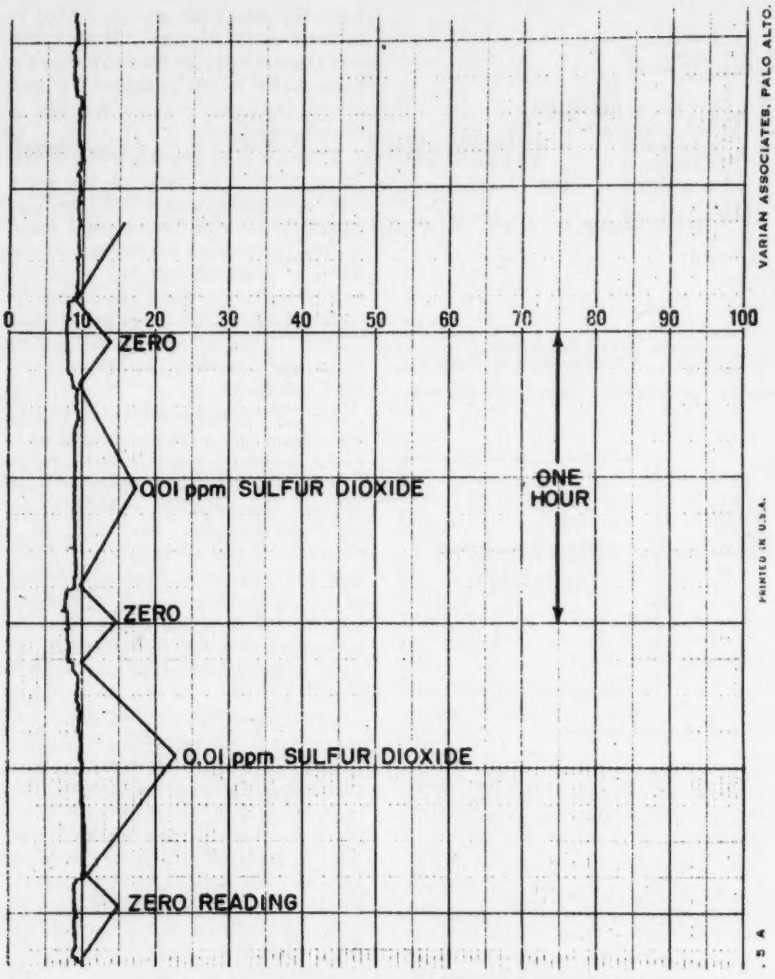

Fig. 4. Typical record obtained at 0.01 ppm sulfur dioxide.

of the zero level, however, this would not be possible unless zero readings are recorded at frequent intervals.

In the laboratory, it was noticed that line voltage variations seemed to affect the stability of the instrument, so a Sola constant voltage transformer of 500 v-a capacity was used for actual field operation. The vacuum pump which supplied suction was connected directly to line voltage, since the starting load of the pump motor exceeded the capacity of the transformer. All portions of the instrument except the vacuum pump were connected to the output of the constant voltage transformer

For field use, the instrument was mounted in a small trailer. The entire unit could then be moved readily and parked wherever 110–v power was available. It was moved at weekly intervals, to obtain records of sulfur dioxide concentration in different sections of the community. The instrument has been inspected only twice weekly for approximately five months, and has operated satisfactorily with only this small amount of attention. At one time a power failure occurred and the power was off for several hours. When power was available, the Titrilog started up, leveled off to a normal operating condition in approximately one hour, and continued to operate satisfactorily with no adjustment.

Maintenance troubles have been very minor, considering the small amount of attention which has been given the instrument. After an initial period of one month during which several adjustments were made and some of the vacuum tubes in the amplifier replaced, the only item which had to be replaced was a mercury cell in the recorder. At a chart speed of 2 in/hr, one recorder chart lasts for approximately three weeks. The dry cell battery used has a service life of two to three months.

Summary

A Titrilog instrument was modified for field use, to increase the sensitivity by a factor of ten. The noise level was reduced to a satisfactory level by an electronic filter. Drift of the zero point was the greatest difficulty encountered, and occasionally no record was obtained when the zero point drifted off the scale for brief periods. No excessive maintenance problems were encountered in five months' operation.

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APCA Has New Printer

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Some Measurements of OXIDANT LEVELS *at Remote California Sites*

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As part of a long-range study of natural levels of trace substances common to both polluted and unpolluted atmospheres, a series of measurements was undertaken in the coastal areas of California. The investigation was jointly supported by the Department of Public Health, State of California, the U. S. Weather Bureau, and the Public Health Service.

Background oxidant levels, presumably caused by natural ozone, can have importance for a number of reasons: (1) they represent the lower limit attainable by air pollution control; (2) natural ozone may enter into reactions with organic pollutants to form toxic end products,[1] and (3) if these concentrations vary sufficiently with meteorological conditions, a pollution incident may well be intensified or moderated, depending on whether it coincides with a natural maximum or minimum, respectively.

Hence it was deemed desirable to determine (1) the normal level of oxidant at remote Pacific Coastal sites, (2) the size and frequency of deviations from normal, and (3) the meteorological conditions concomitant with these deviations. It was also necessary to attempt to determine the trajectory of the air sampled, since little information was available on the persistence of oxidant from urban sources. The meteorological aspects of the problem are being reported separately.

Sampling Sites

The locations (Fig. 1) employed in the study were selected for two basic purposes. First, several sites sufficiently remote from major urban centers were chosen so that true background ozone concentrations could be measured frequently and some idea of spatial and temporal variability gathered. Mt. Hamilton, Crescent City, and Point Piedras Blancas were in this group. Second, key sites near cities were desired so that influent air could be monitored shortly before being subjected to their pollution. These locations included S. E. Farallon, San Nicolas, and San Clemente Islands near, respectively, San Francisco, Los Angeles, and San Diego.

Mt. Hamilton is situated on a 4200-ft peak, the highest in the immediate vicinity, about forty miles southeast of Oakland and San Francisco. At this elevation, it lies above the almost permanent temperature inversion present at many places along the California coast, and air sampled there was thought to be reasonably representative of that elevation, uncontaminated by San Francisco Bay Area pollution. It is the site of the University of California's Lick Astronomical Observatory and is the only station of the group appreciably above sea level.

Crescent City, California, is directly on the seacoast a few miles from the Oregon border. The town has a population of two to three thousand, and there are no comparable settlements within fifty miles in either direction along the coast. The principal industries are lumbering and fishing, and local air pollution due to sawdust burners unfortunately was sometimes evident in the air-borne particulate samples collected there. A few miles to the east of Crescent City the coast mountain range attains elevations of several thousand feet and acts as a barrier to direct westerly wind flow. The sampling was performed at the U. S. Coast Guard Lighthouse just seaward of the town, where the nearby rocky shore causes considerable surf.

Point Piedras Blancas is also a U. S. Coast Guard Lighthouse located directly on the coast, approximately halfway between San Francisco and Los Angeles. The nearest municipality of more than a hundred inhabitants is the coastal Monterey area about seventy miles to the north. The predominant wind flow at Piedras Blancas parallels the coast because the mountains rise precipitously from the surf to several thousand feet.

Southeast Farallon Island lies about thirty miles west of the Golden Gate. Its longest dimension is no greater than a third of a mile, and its maximum elevation is a cuspoidal peak, 360 ft above mean sea level. A few smaller islets lie close by and generate copious amounts of surf. Eight Coast Guardsmen live on the island and maintain 24-hr watch at the building where the sampling was carried out. The predominant wind directions at this site are from the northwest quadrant, away from the San Francisco Bay area.

San Nicolas Island is in a U. S. Naval restricted area approximately seventy miles offshore west-southwest of Los Angeles. The island is about eight miles long, three wide, at 800 ft maximum elevation, and lies with its major axis in a nearly northwest-southeast direction. The elevation of the sampling point was 570 ft. Several hundred naval personnel occupy the island but there are no local pollution sources of any importance.

San Clemente Island is also occupied exclusively by the military. It is about eighteen miles long, four wide, 1900 ft high, and lies sixty miles south of Los Angeles. The sampling location was in a cove on the northeast side of the island at an elevation of about 200 ft. Living quarters for the military personnel were nearby, but they were believed to cause negligible contamination.

Sampling Methods Employed

Depending on such factors as interest in detail, site accessibility, and equipment available, two different sampling methods were employed. On the two

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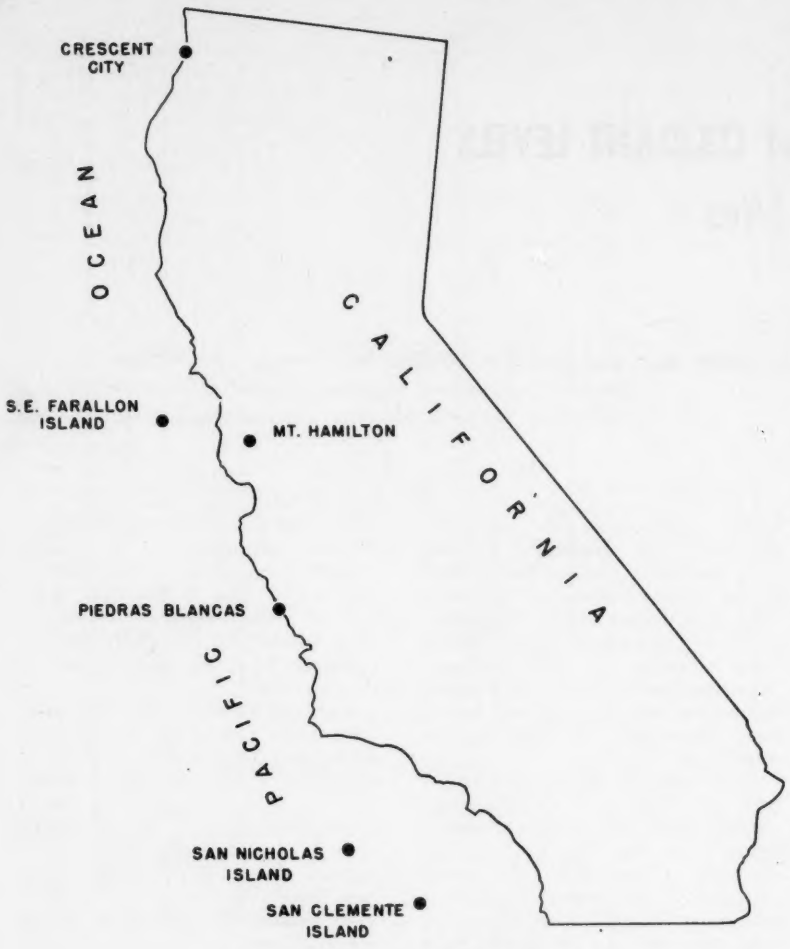

Fig. 1. Location of sampling sites.

channel islands, San Nicolas and San Clemente, Beckman continuous oxidant recorders with 20% potassium iodide reagent were used. These machines were provided for the four-month period of operation by the Los Angeles County Air Pollution Control District and serviced by U. S. Public Health Service personnel. Periods of intensive manual sampling of three-to-four days' duration to assess diurnal variation of ozone at four of the sites were also performed. For this work, phenolphthalin reagent[2] exposed in glass bubblers was used; concentrations determined by it may be compared only approximately with those measured by the continuous recorders.[3] A ten-minute average concentration was determined by this method every twenty minutes from morning to night, and a plot of diurnal variation was made. Once-daily measurements employing this same method were carried out at approximately noon for varying periods of time at Crescent City, S. E. Farallon, Mt. Hamilton, and Point Piedras Blancas. While this single daily test has its greatest significance over a period of years' duration, inspection of the data of a few months is interesting.

The Beckman continuous oxidant recorders used on the channel islands were arranged to measure "oxidant precursor"[4] in part of their sampling cycle. The attachment used for this purpose was similar to that described by L. M. Richards.[4] Automatic valving permitted the recorder to sample direct atmosphere for forty-five minutes of each hour while a by-pass airstream of proper flow rate purged the precursor chamber. For the remainder of the hour, the analyzer drew air directly from the precursor chamber. Identification marks were automatically inserted in the record for each cycle. Fig. 2 shows a typical daily recorder trace with precursor activity in the morning.

Single Daily Measurements

At the three stations where this test was applied—Crescent City, S. E. Farallon, and Mt. Hamilton—the work reported here (Tables I and II) covers widely differing periods. At Mt. Hamilton, the first location to be started, the data covers a period of nearly one year. The observations were made with considerably less than daily frequency, and only 119 days were sampled. During September, October, and November 1956, there is a gap of more than one month in which no measurements were made. However, the data as they stand now are interesting; as the time of operation lengthens, these irregularities will decrease in importance. Mean value for the period, 0.048 ppm, is not strikingly different from commonly accepted surface background concentrations, and may possibly be characteristic of the 4200-ft elevation in general. The maximum of 0.18 ppm and the next highest of 0.14 ppm were determined by use of color standards instead of by colorimeter and may be overestimated. The most probable concentration was 0.02 ppm; about 70% of the determinations were 0.05 ppm or less. The data show a slight tendency to be lower during the winter months, but more than one year's operation will be needed to confirm this.

A more sustained sampling effort was made at Crescent City. Although covering little more than four months, air was tested on 73 days during the period. There is a barely discernible trend toward lower values during the winter months, and again more than one year must be examined to confirm this observation. The mean value of 0.029 ppm for the period is probably significantly different from that of Mt.

Table I—Frequencies of Occurrence of Daily Oxidant Concentration by Phenophthalein Method

Concentration, ppm	Crescent City 9-21-56 to 1-31-57 (73 days), %	S. E. Farallon 12-12-56 to 1-31-57 (34 days), %	Mt. Hamilton 3-15-56 to 1-31-57 (119 days), %
0.0	1	0	1
0.01	7	0	4
0.02	38	0	20
0.03	26	3	14
0.04	15	3	17
0.05	10	23	12
0.06	1	15	9
0.07	1	6	8
0.08	0	23	3
0.09	0	9	4
0.10	0	6	3
0.11	0	0	3
0.12	0	3	0
0.13	0	6	0
0.14	0	0	1
0.15	0	0	0
0.16	0	3	0
0.17	0	0	0
0.18	0	0	1

Table II—Daily Oxidant Concentrations by Phenophthalein Method

Location	Period	No. Days	Maximum, ppm	Minimum, ppm	Mean, ppm	Trend
Crescent City	9-21-56 to 1-31-57	73	0.07	0.0	0.029	Slight decrease toward winter months
S. E. Farallon	12-12-56 to 1-31-57	34	0.16	0.03	0.075	Insufficient data
Mt. Hamilton	3-15-56 to 1-31-57	119	0.18	0.0	0.048	Slight decrease toward winter months

Hamilton and is decidedly background concentration. Again, the modal value is 0.02 ppm and 98% of the concentrations are 0.05 or less. It is well to remember that the scantiness of the data prohibits any estimate of annual variation and that daily peak values of 0.10–0.12 ppm were found in July, 1956, during the intensive sampling periods described later.

Because of their fragmentary nature, the results of the first month and a half at S. E. Farallon are included only as a matter of passing interest. The maximum value of 0.16 ppm and rather high average of 0.075 ppm certainly demonstrate the occurrence of unexpectedly high oxidant at this site. February and March, while not considered here, do not appear to change this picture. However, since wind trajectories are not considered here, it is possible that at least the highest values may be the result of pollution from the Bay Area.

Intensive Spot Check Measurements

At the beginning of the study it was realized that, while once-daily oxidant sampling several times a week would considerably increase the existing information about the background pollutant levels at these remote sites, it would actually provide only the barest information, with no indication of peak values or diurnal variation. As both a temporary and an exploratory measure, pending availability of more complete instrumentation, four of the remote sites (Crescent City, Mt. Hamilton, Piedras Blancas, and San Nicolas Island) were visited for periods of intensive manual sampling for total oxidant. The aim of detecting diurnal variations required frequent measurements, and a schedule of one sample every twenty minutes was selected. The period involved for all work was June 12 to July 27, 1956. Sampling began at approximately 0800 and continued as late as 2300, or until the oxidant had dropped to about the same level as that measured early in the morning. Duration of the work at each station was three to four days.

At Mt. Hamilton and Piedras Blancas, the first two locations sampled, some data were lost because of technical difficulties. However, enough measurements were made to indicate the nature of the diurnal fluctuations on the days tested. Throughout the day, values appeared to fluctuate randomly at a low level approximating the expected background concentrations of ozone. No distinct daily peaks were evident.

At the other two sites, however, completely different characteristics were discovered. Beginning July 10 on San Nicolas at 0800, the oxidant concentration rose steadily from about 0.05 ppm until it reached a maximum of 0.10 ppm at 1300–1320. From that time until 2020 it declined to approximately 0.03 ppm. The following day the process was repeated, but a late afternoon high of more than 0.14 ppm was reached at 1600 and the last measurement on that day remained at 0.07 as late as 2020. On the next day, the reading had reached almost 0.09 when work was terminated at noon. At Crescent City a similar pattern occurred but all values were somewhat lower; the daily maxima for the three-day operation were 0.13, 0.08, and 0.11, all recorded well into the afternoon.

While both the San Nicolas and Crescent City results clearly demonstrated that peaks of total oxidant concentration could occur at these locations, generally considered remote from major municipal pollution, the diurnal variations were rather smooth and unlike the high, sharp peaks of oxidant found in Los Angeles. It is not possible to prove that all of these high oxidant levels had other than natural origin, as meteorological data are too sparse for unequivocal determination of air trajectories. The lack of such diurnal variation during the Mt. Hamilton and Piedras Blancas tests could be due to the short period of observation.

Four Months' Data from Two California Offshore Islands

A summary of the range of values of total oxidant concentration found by continuous recorder on the channel islands is given in Table III. The recorders were in place for 125 days; loss of data due to instrument malfunction was 25% at San Nicolas and 10% at San Clemente. The average daily maxima for both of the sites are greater than is normally considered background for such remote locations. The range of values measured during the operation is surprising as it goes from zero at both places to the high for the period, 0.38 ppm, at San Nicolas. A few times each of the recorders registered a negative reading (arbitrarily taken as daily minimum of zero), usually associated with precursor activity and in the early morning. The significance of this behavior is not presently clear to the authors.

Frequencies of daily maximum oxidant concentrations (Table III) for the islands show both distinct similarities and differences. At both sites the daily maxima most frequently found were in the range 0.05–0.10 ppm, or probably lower than comparable Los Angeles figures for the same time. The next lower range, 0.0–0.05 ppm, occurred on an appreciable number of days in both cases, but with decidedly greater frequency at San Clemente than at San Nicolas. This disparity confirms the general impression developed during the work that San Clemente oxidant was usually lower than that at the other site. The salient difference between the two stations lies in the higher concentration ranges, since 7% of the San Nicolas maxima lie in the range 0.20 ppm and above, and the San Clemente recorder registered no higher than 0.18 ppm at any time during the period.

Table IV confirms the previously noted differences between the daily oxidant march of urban pollution and that found on the channel islands. The table clearly shows the "flat" nature of diurnal variation at the islands by the fact that on more than half of the days in question, the oxidant value remained at half the daily maximum or above for

Table III—Frequencies of Daily Maximum Oxidant Concentration 9-13-56 to 1-15-57

Concentration, ppm[a]	San Nicolas (90 days), %	San Clemente (114 days), %
0.0 to 0.05	14	28
0.05 to 0.10	48	52
0.10 to 0.15	23	16
0.15 to 0.20	8	4
0.20 to 0.25	3	0
0.25 to 0.30	3	0
0.30 to 0.35	0	0
0.35 to 0.40	1	0
Absolute maximum	0.38	0.18
Average daily maximum	0.10	0.07
Average daily minimum	0.03	0.02

[a] All concentrations are given by volume.

Table IV—Frequencies of Duration of Oxidant at a Value ≧ Half Daily Maximum 9-13-56 to 1-15-57

Daily Duration, %	San Nicolas (90 days), %	San Clemente (114 days), %
0 to 10	3	8
10 to 20	3	7
20 to 30	6	7
30 to 40	3	7
40 to 50	3	9
50 to 60	14	6
60 to 70	7	5
70 to 80	6	10
80 to 90	2	11
90 to 100	53	30

periods of time greater than sixteen hours. The daily maxima generally were not sharp peaks, in decided contrast to urban records. The complementary information in Table V demonstrates that once the concentrations did reach relatively high values they often tended to remain high for some time.

In Los Angeles and San Francisco, the time of maximum intensity of oxidant concentration in smog is approximately noon, with peak values rapidly reached from much lower nighttime levels. Tables VI and VII illustrate again the difference between normal behavior of urban and island oxidant. At both locations a substantial proportion of all of the maxima occurred in the afternoon, and on a significant number of occasions the maxima at both locations took place after 1800. On the severe days this fact is borne out with still more clarity. Of the fourteen days on San Nicolas with daily maxima of 0.15 ppm or greater, these values were recorded on eight of them at 1600 or later. Of the five days in this category on San Clemente, the times were generally earlier, but all were after 1300. A few times on San Nicolas the large daily maxima took place at 0600 to 0700, but at neither location was this period the favored time. However, one season may be insufficient correctly to characterize oxidant concentrations on these islands.

A detailed study of meteorological conditions attending the oxidant maxima will be published elsewhere.[5] The findings may be summarized here, however, by stating that some of the high values—especially those preceded by precursor activity—appeared to originate in urban areas. However, for a significant number of cases, no continental source could be proved.

Some measurements of "oxidant precursor" have been made previously,[6] but the current state of knowledge does not permit their quantitative interpretation. Precursor was detected on twelve occasions on San Nicolas and on seven occasions on San Clemente, as shown in Table VIII. It invariably appeared in the early morning; with a few exceptions, it disappeared before 1200. Since it is not possible to attach quantitative significance to these values, they are indicated merely as "slight" or "marked" in the table. It may be noted that there is a tendency for "marked" occurrences to be common to both islands.

Table V—Frequencies of Duration of Oxidant at a Value ≧0.10 ppm 9-13-56 to 1-15-57

Daily Duration, %	San Nicolas (90 days), %	San Clemente (114 days), %
0	66	83
>0 to 10	16	10
10 to 20	3	6
20 to 30	4	1
30 to 40	6	0
40 to 50	2	0
50 to 60	2	0
60 to 70	0	0
70 to 80	0	0
80 to 90	0	0
90 to 100	1	0

Table VI—Frequencies of Times of Occurrence of Daily Maximum Oxidant Concentrations 9-13-56 to 1-15-57

Time of Occurrence (PST)	San Nicolas (90 days), %	San Clemente (114 days), %
Early morning (00 ≦ t <09)	18	19
Late morning (09 ≦ t <12)	7	21
Early afternoon (12 ≦ t < 15)	32	25
Late afternoon (15 ≦ t < 18)	23	18
Early evening (18 ≦ t <21)	10	11
Late evening (21 ≦ t < 24)	10	6

Table VII—Frequencies of Times of Occurrence of Daily Maximum Oxidant Concentration 0.15 ppm and Above 9-13-56 to 1-15-57

Hour Beginning (PST)	San Nicolas (14 days), days	San Clemente (5 days), days
0600	1	—
0700	1	—
1300	3	3
1400	1	1
1600	1	1
1700	1	—
1900	2	—
2000	2	—
2200	1	—
2300	1	—

Conclusions

It has definitely been demonstrated that high oxidant levels occur at sites generally considered sufficiently remote to be free of urban pollution. In some cases it appeared that polluted air was, in fact, being sampled, despite its extremely long trajectory from the nearest urban source. There were, however, other cases in which a natural origin for the oxidant could not be excluded.

Further work is indicated in two directions: (1) Sites sufficiently remote to be truly free of urban influence must be studied, and (2) factors should be investigated which favor extremely long-distance travel of urban air without dilution.

Should it still prove impossible to exclude natural sources for high oxidant levels such as those reported here, research should be undertaken to delineate the mechanism of the production of such concentration near sea level.

The present work is being continued.

Summary

Measurements of surface oxidant concentrations at six California sites

Table VIII—Times of Occurrence of Precursor Activity 9-13-56 to 1-15-57

San Nicolas Day	San Nicolas Time (PST) and Degree of Activity	San Clemente Day	San Clemente Time (PST) and Degree of Activity
11-3-56	0600 to 0730 (slight)	10-25-56	0300 to 0730 (slight)
11-7-56	0700 to 1030 (slight)	11-6-56	0600 to 1020 (marked)
11-9-56	0300 to 0900 (marked)	11-16-56	0620 to 1330 (marked)
11-10-56	0300 to 0830 (slight)	11-17-56	0300 to 1200 (marked)
11-15-56	0300 to 0900 (marked)	11-26-56	0500 to 1230 (marked)
12-8-56	0500 to 1700 (slight)	12-24-56	0600 to 0830 (slight)
12-16-56	0400 to 1300 (slight)	1-6-57	0710 to 0930 (slight)
12-17-56	0700 to 1500 (marked)		
12-18-56	0440 to 1400 (marked)		
12-19-56	2300 to 0100 (slight; next day)		
12-23-56	0400 to 0900 (marked)		
12-26-56	0300 to 0800 (slight)		

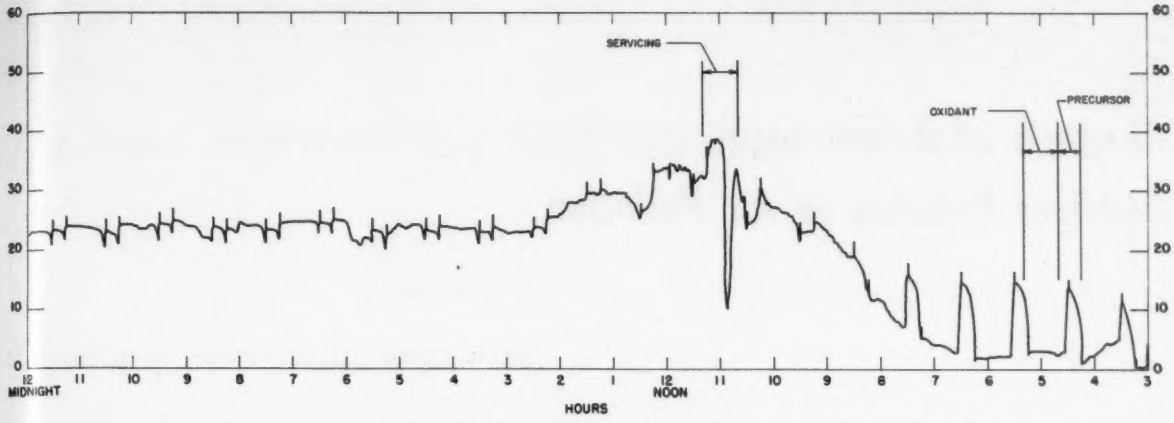

Fig. 2. Record of oxidant-precursor recorder on San Nicolas Island, November 15, 1956, showing morning precursor activity. Ordinate is recorder response in arbitrary units; the midday peak is approximately 14 pphm.

remote from major municipal air pollution are reported. Pertinent environmental features of these sites such as proximity to the ocean and populated areas, altitude, and wind flow are discussed. Both the manual phenolphthalein and automatic recording potassium iodide methods were used. Procedures varied among the different sampling sites and included once-daily manual determinations, periods of intensive spot-check work for several days in succession, and operation of continuous recorders on two offshore islands for four months. Frequency distributions of daily peak values, times of maxima, durations, etc., are presented and discussed. Unexpectedly high concentrations of oxidant were occasionally found at each remote site, but it was not possible to attribute these to natural sources with complete certainty.

Acknowledgments

This study was made possible through the co-operation of different agencies and individuals. The California State Department of Public Health, where the work was headquartered, supplied the most sustained support. The Los Angeles County Air Pollution Control District furnished the continuous oxidant recorder and supplied facilities for its modification. Meteorological studies were made by G. E. Holzworth, U. S. Weather Bureau. Transportation to certain remote areas and access to sampling sites, were made possible by the co-operation of the U. S. Coast Guard and Navy. Persons who assisted in planning the over-all study of which this work is a part include Dr. Leslie A. Chambers and Walter Hamming, Los Angeles County Air Pollution Control District; Dr. Morris Neiburger, University of California, Los Angeles; Dr. Lewis H. Rogers, Air Pollution Foundation; Dr. Richard D. Cadle, Stanford Research Institute; Dr. W. D. Crozier, New Mexico Institute of Mining and Technology; Dr. A. J. Haagen-Smit, California Institute of Technology; Benjamin Linsky, Bay Area Air Pollution Control District; Dr. Ralph Stair, National Bureau of Standards; Frank M. Stead, State Department of Public Health, California; Bernard D. Tebbens, University of California School of Public Health; Jacob F. Cholak, Kettering Laboratory; Dr. W. C. L. Hemeon, Hemeon Associates; Dr. Christian E. Junge, Geophysics Research Directorate; Dr. Lester Machta U. S. Weather Bureau; Dr. E. R. Stephens, Franklin Institute; A. H. Woodcock, Woods Hole Oceanographic Institution; Dr. E. K. Harris and R. C. Wanta, Robert A. Taft Sanitary Engineering Center.

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Abstracts of Recent Legal Decisions Relating to Air Pollution

LEGAL COMMITTEE, Air Pollution Control Association

The first of the abstracts of legal decision, prepared by our Legal Committee of which William Foster is chairman, appeared in the November, 1958 issue of the Journal of the Air Pollution Control Association. Similar abstracts will be a regular feature in future issues.

The People v. Wherry,

(Appellate Department of Los Angeles Superior Court, No. C 244428. Not formally reported.)

Defendant was charged in two complaints with discharging "excessive smoke" in violation of Section 673.5 of the California Vehicle Code, which provides:

> "No motor vehicle shall be operated in a manner resulting in the escape of excessive smoke, flame, gas, oil or fuel residue."

The complaint was dismissed in the Los Angeles Muncipal Court on the ground that the cited section was unconstitutional. The term "excessive smoke" was held too indefinite, vague, and uncertain to satisfy the requirements of due process of law. The Municipal Court further declared that the statute did not purport to prohibit the discharge of all smoke, but set up no reasonably ascertainable standard by which a driver could determine how much smoke his car could emit without committing a violation of the criminal law. The Muncipal Court then cited and quoted from *People v. San Pedro Lumber Company, et al.*, Cr. A. 2677, a 1951 Municipal Court case, which held that an ordinance making it a criminal offense to discharge "any unnecessary or unreasonable smoke, dust, soot, or fumes" was unconstitutional.

Superior Court HELD:

Reversal, and stated: "Defendant centers his attack on the word 'excessive.' To determine that the use of the word 'excessive' does not make the section vague or uncertain we do not need to go beyond *Smith v. Peterson* (1955), 131 Cal. App. 2d. 241. There the court held constitutional V.C. 673, which requires that a motor vehicle when operated on a highway shall be equipped with an adequate muffler 'to prevent any excessive or unusual noise.' We commend a reading of the entire opinion to any who claim that the word 'excessive' makes V.C. 673.5 vague and uncertain. See also *People v. Pawson*, (1946), our CR. A. 2198."

Guttinger v. Calaveras Cement Company,

160 A.C.A. 493, 325 P. 2d. 145

(California District Court of Appeal, Third District, May 14, 1958).

Plaintiffs brought an action at law for damages caused by the escape of dust and chemicals from defendant's cement plant onto plaintiffs' land. Some 10 years previously, plaintiffs had secured damages and an injunction against defendant in an equitable proceeding which was still pending. The injunction required defendant to maintain precipitators and prohibited it from discharging from its stack more than 13% of "all flue dust and/or raw mix in powdered form which would, or could, be emitted or discharged . . ."

In the trial court, *judgment was for defendant* on the grounds that there was a prior action pending, that the prior action was res judicata as to issues in this case, and that the plaintiffs, having to pursue an equitable remedy in the prior case, were estopped from bringing an action at law.

HELD: Judgment reversed. The court held that this was a continuing nuisance, each repetition of which was a separate wrong for which separate damages and injunctive relief could be granted. But the prior equitable decree, although not a bar to the present action, was a final adjudication that a discharge not exceeding 13% does not cause injury to plaintiffs and is not a nuisance. This finding could be modified only by showing that conditions had changed since the time of the original decree. The court also held that the injunctive procedure was merely an additional remedy and did not estop plaintiffs from pursuing the present action for damages.

Fifty Years BACKWARD *and* FORWARD *in Air Pollution Control**

BENJAMIN LINSKY, Bay Area Air Pollution Control District, San Francisco, California

A few years ago, in 1950, there were many speeches and papers in many fields of interest that reviewed and forecasted events and developments because it was mid-century.

This is a similar review and forecast. The reason is the 50th annual conference of the Air Pollution Control Association. Other reasons and associated ideas were found, after the primary motives of the author and the Air Pollution Control Association led to the decision that this discussion would be held.

The total objective of this discussion was established as being a stimulant to future action to obtain cleaner air.

It is not to contain an encyclopedic review of all applicable knowledge. Neither is it to contain a history of the Air Pollution Control Association or any single component of the generally recognized field of air pollution control such as administration, research, development, or physical application. Instead, the backward looking is intended to sum up as much of the significance of the past 50 years as the author can assemble from his own direct experience and his own learning from the spoken and written experiences of others. The backward looking is also intended to contain such synthesized concepts as this person can develop at this time from these experiences and from the spoken and written concepts of others.

Appropriate specific credits could not be given, even if time permitted, because the author has received extensive verbal communications from thousands of specialists and interested non-specialists during the past nine years and he cannot identify the specific person who conceived an idea or spoke to him about his direct experiences.

This discussion's forward looking, if it is to be useful in stimulating future action to obtain cleaner air, should be more than a forecast of what is likely to occur, *a la* Nostradamus, Edward Bellamy, Jules Verne, Tom Swift, Jack London, Aldous Huxley, George Orwell, and the contemporary science fiction writers. It should, nevertheless, contain similar forecasts that will, in similar fashion, probably, turn out to have been completely mistaken or partially mistaken or woefully short-sighted when re-read 10, 25, or 40 years from now.

It is intended, therefore, that this discussion, as it looks forward, will present concepts, many of them not original with the author, that will help people decide how to act to obtain cleaner air.

Because the author is an active administrator of a community air pollution control program, and lest he be labeled an impractical visionary, it is necessary that he state here, clearly, that the concepts, especially those that tentatively look far forward, are not his proposed program of action for his community. His program of action must develop out of the logic of his community's situation, resulting from the weighing of the many factors and forces that affect design, timing, and movement.

No single community or metropolitan area or region or state or nation has ever obtained as clean an atmosphere for its citizens as air pollution specialists have known how to achieve technically, so far as the author knows. Nor is any area ever likely to achieve such a goal, in the author's opinion. *We ain't farming half as well as we know how, now!* said the farmer.

Neither has any community, metropolitan area, region, state, or nation ever obtained as clean an atmosphere as large numbers (probably a majority) of its citizens would like to have, so far as the author knows.

The spread between technical capability, citizen desire, and achievement can be accounted for by poor communications between people. *It sure takes some people in this man's Navy a long time to get the word,* said the sailor.

During the past 50 years the greatest obstacle to clearing the air has been poor communication of information between people and groups, in the author's opinion.

It is true that much of the poor interchange was due to ignorance and inertia, but it is also true that much of the poor interchange was and continues to be deliberate.

Information about air pollutants and their control (or about anything else) has value to anyone in the world only to the extent that it serves as a basis for future decision for action by people.

Therefore, any deliberate or unwitting interference with the exchange or dissemination of information about air pollutants has led to decisions that had inadequate basis.

I refer to those types of poor communication in the fields following:

First, Documentation: The inadequate organization of systems for recording, storing, and transmitting information for use by those who need it.

Second, Security: The deliberate withholding of data about air pollutants for economic, political, or military defense reasons by persons or organizations.

Third, Semantics: The deliberate or unwitting use of words and numbers that are not clearly defined or clearly understood by the writer-speaker and the reader-listener.

In order to establish a better understanding, at least between those who are occupationally concerned with air pollution control, as a prelude to a better understanding between these air pollution control specialists and the general members of the community, it is essential that words with specific, uniform meaning be used.

To have heard a solid-fuel or metallurgical industry's technical lobbyist speak to a mid-western city council or a north-eastern air pollution conference about the *insignificance of carbonaceous or metallic particles in air pollution* by references to *air pollution in a southwest city where liquid and gaseous fuels only are used* is to have recognized the importance of avoiding the generalized terms. This is necessary if the objective is information leading to understanding leading to action.

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* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2–6, 1957.

Fifty years ago this organization held its first annual conference. It had been organized a year earlier in Detroit, Michigan, as an international group with officers selected from the United States and Canada. Its members were definitely interested in the abatement of black smoke and fly ash from coal burning. The extent to which its members were interested in the metallo-mineral-petronutro-chemical sources and types of air pollutants is not known to the author.

The metallurgical, ore reduction, food and food waste processing and chemical operations had many instances of excessive air pollution. As public minded citizens with interest in a physical science it can be estimated that those in attendance at the first meeting knew a little bit about the first American trans-county boundary air pollution case that had come into focus in the San Francisco Bay Area, where an ore smelter (mineral-metallo) at Selby emitted gases and dusts that damaged vegetation in an adjacent county. This situation is believed by many to have provided the incentive for the earliest intensive technical study of air pollutants in the United States. The studies are still in operation conducted by the American Smelting & Refining Company.

Some of those who attended the first conference may also have been familiar with the chemical air pollutants under regulation, in England, by the Alkali Act.

Most of those who attended the first conference were undoubtedly aware of the air pollutants from the nutro sources that were traditionally labeled *the offensive trades.* The slaughterhouse, the rendering plant, the sewage treatment plant, and the spice manufacturer, among others, were known to cause disturbance to neighbors through air-borne molecular compounds.

It is interesting to note that eyes have been more readily accepted as being publically, officially valid instruments in observations of air pollutants (and many other phenomena) than have the other human senses. This appears to be true whether one is concerned with direct visual observations using a visual comparison standard (the Ringelmann chart or painted surfaces or vegetation or metal or a distant hill), or whether one is concerned with indirect visual observations using the pointer or counter on an instrument meter. Color (where we are involved in the attributes of hue, brightness, and saturation) pattern (as in biological cell microscopy) and turbidity (in air or in liquids) are acceptable visual observations. They are considered more reliable when imitated through photochemical processes that are recorded in two-dimensional photographic models.

The odor sense appears to many to be more readily accommodating, that is, it provides reduced recognition with increased time and intensity of exposure. It is less readily accepted in formal discussions by air pollution specialists. In private discussions and in actual practice, however, air pollution specialists rely heavily on the odor sense.

The sense of touch and the sensations related to eye irritation, respiratoy irritation, and reduced vital (lung) capacity have, similarly, been relied upon in private practice and scorned in public discussion.

During the past 50 years the development of instrumentation has proceeded at an accelerating pace in many technical fields to verify and extend the senses in time, spectrum, and intensity or sensitivity. The use of mathematical logic, aided by mechanized computers, has extended the ability of man to remember, to verify, and to develop relationships between his recorded observations of occurrences.

In a few isolated instances, and by a very few practitioners, there have been developed some special identification and measurement methods solely because of ordinary community air pollutant problems. Many more such methods appear to have been developed because of the special air pollutant problems related to nuclear fission and fusion. Other new measurement developments arose from chemical warfare and long range missile and submarine studies.

It is interesting to note that the development of each identification and measurement technique appears to lead directly to new findings about the undesirable effects of air pollutants and the development of corollary control methods involving procedures and equipment. In contrast, however, many communities appear to operate on the basis that *if you measure and measure and measure the pollutants long enough they will get up and walk away.*

Studies of the effects of air pollutants on human health, as reported in the technical literature now generally available to air pollution specialists and laymen still read remarkably like the 1915 report of the Chicago Association of Commerce Committee of Investigation on Smoke Abatement and Electrification of Railway Terminals, a monumental study of a city's air pollution.

Newer studies are being made about the effects of air pollutants on tissue culture and on the *whole man* in relation to long range submarine operations and manned satellite-interplanetary flight plans.

During the next fifty years one may speculate on many interesting developments.

Because of the improved flow of information between the applied scientist and engineers throughout the world, and between the practical governmental bodies of the world, one can expect more people in more communities to learn that they can obtain clean air, without risking economic disaster from industrial moveouts, simply by insisting on it. There is not, on this date to my knowledge, a single community or larger area that has done all that is known technically or practically about clearing its atmosphere. Los Angeles is closest in most ways.

As the information becomes more widely disseminated as a result of better communication through the migration of people and the activities of regional, national and international government agencies, industries, and voluntary associations like the Air Pollution Control Association, there can be expected to be extended the personal attitude now evident in very few communities in the world that:

Not only is excessive air pollution illegal, but it is also unfashionable and, frequently, extravagantly expensive.

As part of the effective extension of communication, it is anticipated that a truly comprehensive systematizing of knowledge will develop to cover air pollutants, their sources, their transport, their transformation and interaction, their effects, and their technical and administrative control. Indexing, recording, storage, transmission, and retrieval of this knowledge can be expected to develop along the lines of modern documentation and modern indexing. The present handful of bibliographies, manuals, handbooks, and special libraries can thus be expected to be vastly supplemented, at relatively low cost once the design has been established and the back-log brought up to date.

The impact of a well integrated air pollution control program upon a community has been observed to be significant in highlighting and therefore bringing about a clearing up of organized community operations. There is an immediate impact on planning and zoning, health, fire protection, sanitation services, public works, maintenance and engineering, and building inspection activities. Anything less than good co-ordination and adequacy in these government agencies tends to be exposed to a penetrating program of comprehensive air pollution control. The fact that any defects show up, not only in a formal record or report, but in widely observable *sky-writing*, is the key to public requirements for basic corrective action where it is needed. In such instances excessive air pollution will increasingly be recognized as merely another symptom of other problems in community operations. Similar inadequacies in

industrial operations also become exposed for management attention and correction.

As a result of the extensive and ingenious work of many scientists and technicians during the past 17 years in carrying out the brilliant concepts made by a few scientists during the past 50 years, much of it paid for by military and defense funds, it is now scientifically possible to do almost anything one wishes in air pollution control—chemically or physically—if one will pay the price in money and inconvenience.

The types of technical control procedures and equipment that have been developed to stop the emission of radioactive gases, as well as dusts and droplets (visible, microscopic, and submicroscopic) from nuclear operations will be increasingly applied to the more common production processes, bulk power producing equipment, and transportation equipment.

One may expect to see ratios of both capital and operating costs of the order of ½% to 5 or 10% for air pollution control to the total involved. These ratios may well be as routinely scheduled (and debated) as are the United States Internal Revenue depreciation schedules.

The first findings of this International Geophysical Year may well, on retrospect 50 years from now, mark the end of an era of grouping for atmospheric comfort in small neighborhoods and the start of an era that is equally concerned and capable of dealing with the practical and usable characteristics and preservation of local, regional, continental, terrestial, and planetary atmospheres. The concern over the black smogs of London, St. Louis, Liege, Pittsburgh, and Donora and the concern over the blue and mud colored smogs of every metropolis in the world will undoubtedly be cleared away to be replaced by the concern over the electronically detectable, invisible clouds of radioactive gases and submicroscopic particles around the world and between the planets.

As the combustion economy is displaced by the nuclear-chemical economy, concern about soot and fly ash will undoubtedly be replaced by concern over Strontium 90 and radioactive meteorites.

It is more difficult to foresee the changes in air pollution from the production of food, flowers, and lumber.

Color, shape, pattern, texture, and flavor have such importance to people that it is quite possible we will continue to reserve our factory manufactured foods to breakfasts and desserts, leaving our lunches, dinners, and suppers to be composed largely of non-uniform, field and greenhouse cultured fauna and flora. If this should be so, we may expect to continue to find many, though fewer and larger, agricultural operations carried on with a greater incidence of soil-skin coating and subsurface irrigation. The agricultural wastes may be expected to be mined more extensively rather than to continue to be vaporized, or leached out as they are at present in considerable degree.

Food preparation, whether industrial, commercial, or domestic, may similarly be improved for retention of flavor and development of color, pattern, and texture by quick heating and quick cooling. The quick heating, along with the clearing of surfaces by vacuum, ultrasonic, electrostatic, or detergent transfer, may be accompanied by the transport and disposal of wastes through underground hydraulic transport for subsequent centralized community treatment, salvage, and storage. Such storage, generally involved in sewage disposal now, may be mined far more intensively with new extractive and synthesizing techniques.

Personally directed transport that is now carried out in such a way that it is a major source of air pollutants and death by impact cannot be expected to be fully replaced by mass transport unless man's psyche—his emotional makeup—is rearranged in a fashion that contemporary man would consider dull and drab. Other forms of personally directed transport will use, more intensively, the soft lanes of the air instead of the unyielding lanes of the ground. Combustionless stored or remotely transmitted energy will undoubtedly displace the incomplete combustion power sources now used.

The processing of fresh chemicals and minerals and the secondary processing of used chemicals and used minerals can be expected to be carried out in larger, better engineered plants where instruments rather than men feed back the observations needed to vary the operating procedures. With such integrated operations, popularly called automation, the equipment requires such a high degree of atmospheric cleanliness that the incentive to clean the exhaust air is extensive.

It is now not unusual to install an intake air cleaning system costing $500,000 at a steel mill to protect one room of electrical gear against air pollutants produced by the mill itself and a few neighboring sources of air pollution. Similar intake air cleaning systems being installed at metal painting, metal plating, large air compressors, and chemical and petroleum processing operations also indicate the need for cleaner atmospheres than ordinary man has considered necessary for his own well-being.

The world's population is increasing for many reasons. The concentration of population in smaller and larger cities, and the growth of tremendous metropolitan ranges will increase the air pollution concentration potential of each community involved, requiring air pollution control to a degree and over sources now considered unimportant by many air pollution specialists. This factor may be illustrated as follows:

"A man stands in the center of a 10 acre island that is a field of sod. He strips 10 square feet of sod away from the earth around him. A 10 mile wind blows. The tops of the man's shoes become dusty.

"The man removes the sod from all 10 acres of his island. A 10 mile wind blows. The same amount of sizes of dust are emitted from each square foot of bare earth as before. But now he is completely enveloped by a choking cloud of dust.

"The air that now reaches the man is hundreds of feet farther from the point where it was clean, than before, because it has picked up dust from hundreds of feet of dust emission source.

"The man's visitor, sitting in a rowboat at the downwind beach of the island, didn't notice the dust from the 10 square feet of bare earth, but he was even dustier than the islander after the whole island was bared."

As cities grow and touch each other for 20 miles, 50 miles, or 800 miles in the United States, as had happened in England's Black Belt years ago, the frequency of intensive air pollution and the intensity of infrequent air pollution increases, even while the air pollutants from individual sources are reduced.

The planning needs of the future air pollution control standards will undoubtedly be met by the development of mathematical models for each inhabited area of the country by the use of high speed computers and large volume data storage equipment. Terrain factors and micro-climate factors will establish patterns into which will be introduced air pollutant load factors. Verification of the adequacy of the mathematical models will be increasingly developed by measurements of natural tracers, artificial tracers, as well as current air pollutant loadings.

The load factor will include detailed quantity and identification of type, size, and potential detrimental effect of each emission of polluting materials from each source.

The land use planning function and the air pollution regulation planning function together, will be supplied with atmospheric load predictions just as telephone companies are provided with telephone circuit traffic predictions today.

The possibility that some air pollutant concentrations may reach levels that are critically high over tremendous areas, even over the entire world, has already led to requests for international

standards of emission to override local standards. The mathematical model work on some pollutants is undoubtedly well advanced already, according to security-cleared reports.

The increases in air pollution effects that have already occurred have led to expanded study, especially research at national level, by governmental agencies, industrial groups, and semi-public organizations.

The results of these studies, as they are disseminated, will encourage the open demand by citizens in more areas for cleaner air as the air becomes increasingly polluted because more people are living and working closer together. The fact that many of these citizens have managerial and technical responsibility for the larger private and public sources of air pollutants will not be a deterrent. Instead their dual status will assist in the development of technical and administrative methods of reducing the emission of air pollutants from the smaller public and privately controlled sources.

Design and operational performance commercial standards that were adequate for national and individual economy will be revised for air pollution reasons. Exhaust emission standards for domestic oil burning furnaces may be expected to be modified in the foreseeable future in the same way that domestic incinerator standards are being modified now even in well-ventilated cities. The poorly ventilated cities and those covering tremendous areas may well extend their controls to smaller and smaller individual operations while, at the same time, they establish more rigid requirements for the larger operations.

The older fears and threats of industrial move-outs, when air pollutant controls were planned have already proved themselves insignificant. As more citizens and their elected representatives learn that bad-mannered industries drive out and keep out well-mannered industries, and as more of the traditionally bad-mannered industries have learned that they can become better citizens as they clean up their air pollutants at a small percentage of their capital costs and operating costs, the administration of air pollution control programs will probably become increasingly regional and increasingly technical in order that the control be more precise and more equitable.

The higher costs of cleaning gases and submicroscopic dusts and droplets will require more critical determinations of effects, causes, and emissions from sources. The trained eye and nose and the educated, experienced mind will be supported by more instruments in the field and in the laboratory.

The fact that gases and submicroscopic particles travel greater distances than do the larger dusts and droplets that fall out near the source will lead, increasingly, to regional air pollution control administration.

Public support for such loss of local sovereignty will increase because of the reports of formal studies and also because increased personal mobility by ground transport and by air transport will permit more of them to observe trans-boundary air pollutant effects with their own senses.

The forms that air pollution control standards and regulations will take are subject to speculation. As it becomes more widely recognized that many thousands of small sources may add, in total, as much as a few large sources to an area-wide air pollution effect, there may develop patterns of conflict similar to those surrounding taxation, with full or partial exemptions, open or hidden subsidies, and well understood variations based on ability to pay for control, technical ability to control, and administrative ease of control.

It can be expected that the interactions of technical factors relating to air pollution will be easier to trace and define than the interactions of taxation economics. Some specific air pollution problems may possibly exist in some areas under some weather conditions even after doing everything that is technically feasible, but this is not known, yet, anywhere. For other air pollutant situations it can be expected that the exact form that legal regulations will take, although based on technical fact, will be finally determined by the political judgment of those with legislative responsibility for the area of jurisdiction.

Present voluntary standards and government regulations follow many patterns:

Limits on the concentration of a pollutant in such terms as lb. of pollutant/lb. of exhaust gas emitted.

Limits on the rate of emission of a pollutant/unit time/point of emission, in such terms as lb. of pollutant/hr./stack.

Limits on the rate of emission of a pollutant/unit weight of material processed, in such terms as lb. of pollutant/lb. of material processed.

Limits of the demonstrable effect of the pollutant on visibility at the point of emission, in such terms as Ringlemann shade or equivalent opacity.

Limits on the demonstrable effect of the pollutant on people, the things they own, or the things they like to do, translatable, usually, to words of judgment but, in some instances, to specific number measurements of lb. of fall-out/unit time/unit area or the resultant concentration of a pollutant in air or in vegetation or in other material at the receiving point.

Other standards or regulations specify the design of the method or equipment involved or establish a ratio of cleaned to uncleaned pollutants in the exhaust stream.

As more studies are reported publicly and as more individuals and groups publish their experiences and as more of those in the field formulate and disseminate their concepts more systematically and definitively than has been done in the past, there will develop a system of standards and regulations that arise out of the logic of the situations with the few historic *borrowings* of standards well recognized for what they are—expedients that accomplish reductions in air pollution.

It is almost mandatory in such a discussion as this to make predictions about the technical advances that can be expected in the next 50 years.

In spite of industrial and military security restrictions on news of many technical developments, it is safe to say that technically available devices and methods can produce emission streams that are cleaner than is the atmosphere itself. It is also safe to say that for all new processes the same degree of exhaust cleanliness can be obtained technically.

It is proper to state that the new developments in social organization and, especially, communication will be so great during the next 50 years that it is not at all possible to predict the degree to which the technical feasibilities in air pollution control will be turned into legal requirements by communities.

In closing it is necessary to state that:

There is an increasing compaction of people and industries.

There is an increasing output of air pollutants in the form of gases and submicroscopic dusts and droplets.

There is an increasing output of chemically and biologically active types of air pollutants.

There is an increasing need for persons in the many technical groups concerned with air pollutants and their effects to so organize that they will meet face to face and through reports in the literature with a maximum of free exchange of both *giant step* concepts and *baby step* data.

There is an increasing need for the United States Government to take a leadership position within the United States and in the world in which its economic status is so high, by cleaning up the air pollution from the properties, buildings, equipment, fixed and mobile, and the processes that it owns and operates, and reporting fully in the technical literature as to its experiences for the guidance of others now and in the future. There is no question about the technical, financial, or organizational propriety in the specific proposal now,

and because so many of the new developments in high energy fuels, including radioactive ones, are under national security restrictions, as the backlog of conventional problems are cleaned up, the lag between old and new problems will be narrowed so that air pollution problems will not be treated at different technical levels because they are in different security compartments.

Next Issue . . .

APCA Journal will feature articles on the following topics:

1. Measurement of ozone concentration.
2. Odor counteractants for the treatment of stack gases.
3. Reduction and control of air pollution resulting from incineration.
4. Evaluation of absorption sampling devices.
5. Air pollution and health.
6. Cominco operations air pollution control.
7. National Conference on Air Pollution reports.
8. Maintaining controlled fluoride environment in vegetation studies.
9. Air pollution index and its relation to health.
10. Interpretation of air pollution health effects data.
11. Controlling air pollution encountered in pharmaceutical manufacturing.

Proceedings . . .

APCA

51st Annual Meeting

PHILADELPHIA, PA.

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You can save time when planning and save money when buying if you'll send for these DAY dust control bulletins. Each contains valuable information about dust control equipment and systems. Here's general information plus useful technical data and specifications. Ask for any bulletin which interests you or write for them all – they're free. Use this magazine's reader service card or write direct toDAY.

BULLETIN G-579 — Describes the DAY Type "RJ" filter. An all purpose, versatile unit. Bulletin gives operating features, dimensions and specifications.

BULLETIN 573 — Dual-Clone dust separators — noted for their low resistance and high cleaning efficiency. Easy to install, no maintenance, no moving parts.

BULLETIN 576 — "HV" heavy duty dust separator. Rugged construction and lower initial cost than many light gauge galvanized type cyclones.

BULLETIN F-75 — Reverse Jet Dust Filter Facts. Complete with specifications, typical equipment layouts, capacity and performance tables for DAY type "AC" filter.

BULLETIN N-578 — Gives complete information about Style "A" rotary valves. Construction features, specifications, dimensions and applications.

"SCHLITZ DEFEATS DUST" — FOOD ENGINEERING magazine reprint describes all out dust control for 3½ million bushel Schlitz grain elevator. Request Bulletin "Schlitz Defeats Dust."

"EFFICIENT DUST SNATCHERS" — Bulletin describes DAY's part in providing maximum safety and good housekeeping for starch packing building of large food processor.

BULLETIN 510 — DAY Unit Dust Collectors. Complete, low cost unit designed for plants or applications where central dust control systems are not practical.

BULLETIN I-585 — Industrial Fans. Complete with helpful selection charts, capacity tables, dimensions and specifications. Information on special types and arrangements included.

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EQUIPMENT ONLY OR A COMPLETE SYSTEM

The Research-Cottrell score on electrical precipitators for 1958:

32 installations put into operation and completely performance-tested

32 installations meet or exceed guarantees

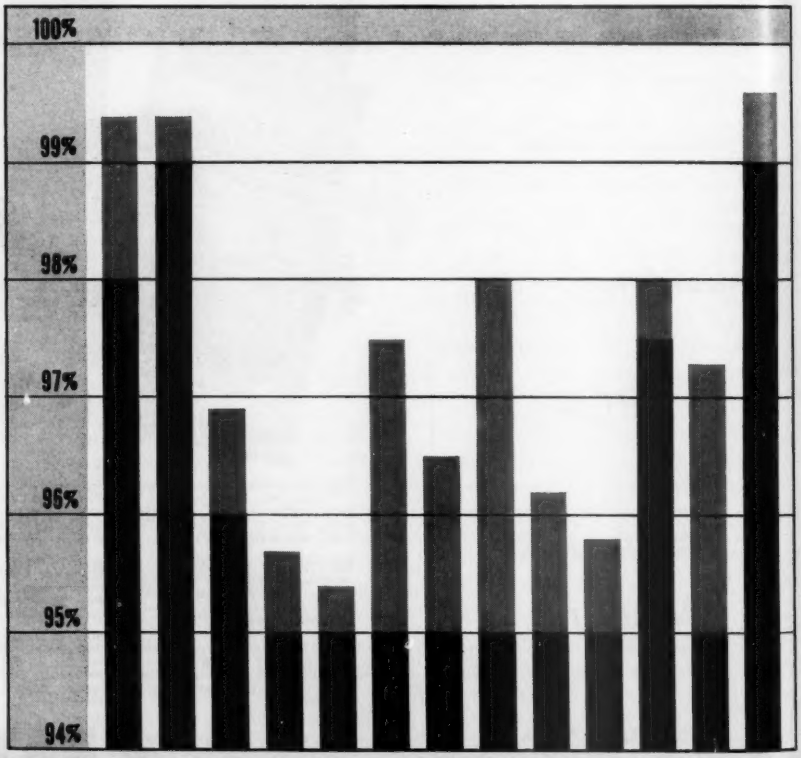
Unprecedented is this record number of 32 installations in one year — all of which met or exceeded their performance guarantees. The chart below shows a number of these installations.

Such a record is no accident. It is largely the result of 1198 years of combined engineering skill and experience — factors which have made Research-Cottrell the undisputed leader in electrical precipitation.

On your next job — if you want the assurance of trouble-free installation and operation, be sure to call on Research-Cottrell.

RC 196

Chart shows 13 typical installations which have exceeded guarantees.
(NAMES ON REQUEST)



Performance over and above your guarantee is a big extra. For example, in the chart, the first bar shows an actual loss of only ¼ of the guaranteed maximum loss. This means a far cleaner gas at no extra cost to you.

Research-Cottrell, Inc.

RESEARCH-COTTRELL, INC. Main Office and Plant: Bound Brook, N. J. • 405 Lexington Ave., New York 17, N. Y.
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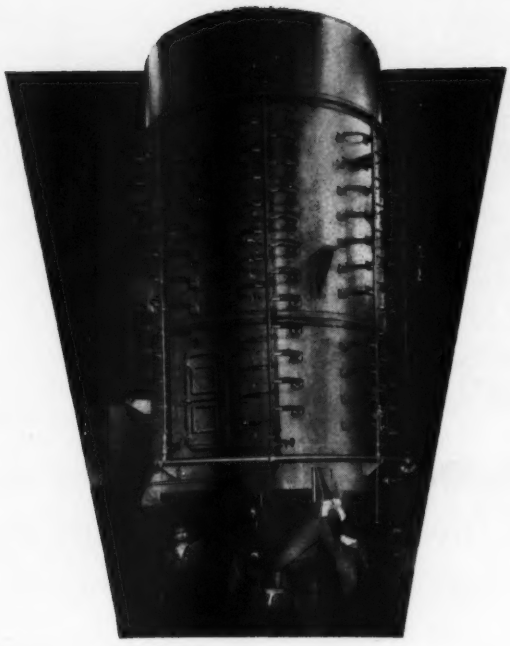
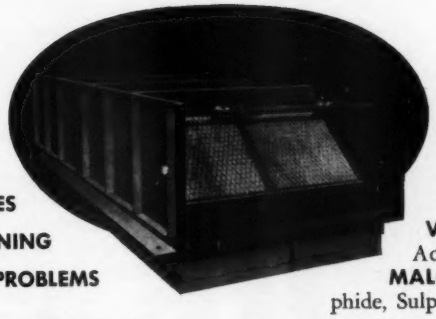


Your AIR POLLUTION and/or GAS RECOVERY Problems SOLVED the EFFICIENT, ECONOMICAL "BUFFALO" WAY!

"BUFFALO" HYDRAULIC SCRUBBING TOWERS

The Ideal Solution for . . .

COKE BREEZE • FUNGICIDES
CHEMICAL ALLOYS • FURNACE FUMES
PHOSPHATE ROCK • LIME CALCINING
GYPSUM BOARD • SO_2 or SO_3 PROBLEMS



"Buffalo" Hydraulic Scrubbing Towers provide maximum efficiency in processing contaminants of the above type by utilizing a highly effective wet centrifugal cleaning method. The result is a compact, dependable unit capable of withstanding high temperatures, sticky, corrosive or abrasive dusts, fumes or gases. For full information on "Buffalo" Hydraulic Scrubbing Towers, contact your nearest "Buffalo" Engineering Representative or write for Bulletin AP-525.

Every "Buffalo" product brings you the extra-value "Q" Factor — the built-in QUALITY that provides trouble-free satisfaction and long life.

"BUFFALO" GAS ABSORBERS

Your Perfect Answer for . . .

ACIDS AND BASES — Hydrochloric Acid, Hydrofluoric Acid, Nitric Acid, Sulphuric Acid, Ammonia • **ORGANIC VAPORS** — Acetic Anhydride, Acetic Acid, Ethyl Alcohol, Methyl Alcohol **MALODOROUS GASES** — Hydrogen Sulphide, Sulphur Dioxide, Sulphur Trioxide.

If you are faced with an industrial air pollution problem involving the removal of soluble gases, vapors and mists from exhaust streams before discharge to the atmosphere, "Buffalo" Gas Absorbers are your most practical solution. "Buffalo" absorption equipment is engineered to handle any required capacity, without adverse effect on efficiency or change in operating characteristics. Your "Buffalo" engineering representative will be glad to recommend the type of Gas Absorber best suited to fulfill your requirements. Contact him, or write us direct. We will be glad to send you full information, including Bulletin AP-225.

"Buffalo"

BUFFALO FORGE COMPANY

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BUFFALO PUMPS DIVISION, BUFFALO, N. Y.

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VENTILATING • AIR CLEANING • AIR TEMPERING • INDUCED DRAFT • EXHAUSTING • FORCED DRAFT
COOLING • HEATING • PRESSURE BLOWING

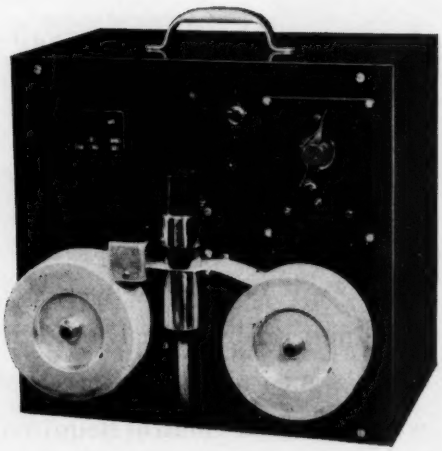
In St. Louis, Missouri

A.I.S.I. SAMPLER measures suspended particulate matter in the atmosphere with minimum time for servicing

St. Louis is one of the outstanding cities that have cleaned the atmosphere, and continuously monitor it to keep it that way.

The city has been using A.I.S.I. Samplers since August 1953, and has found that they require only a few minutes of a man's time a day. In fact, according to J. H. Carter, St. Louis Commissioner Smoke Regulation, "the A.I.S.I. Samplers often operate for several days at a time without attention."

* * *



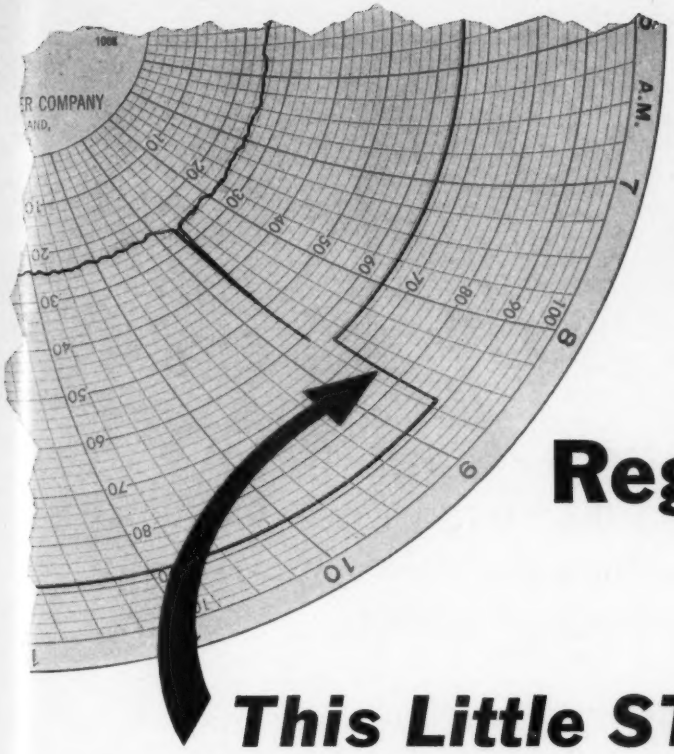
More and more communities are becoming aware of the danger in polluted air, and are establishing measuring and control systems to combat it. *Is your community one of them?*

With the A.I.S.I. Sampler you can sample atmosphere automatically at intervals of ½, 1 or 2 hours, 24 hours a day . . . and the low cost of the A.I.S.I. Automatic Smoke Sampler makes it feasible to locate a large number of them for complete coverage of a geographical area. Its quietness overcomes any objections to its location in or near homes.

Descriptive bulletins on the A.I.S.I. Smoke Sampler and the Hydrogen Sulfide Sampler (which continuously monitors atmospheres having a house paint blackening potential) are available without obligation; and also data on the Spot Evaluator with which the spot samples are evaluated.

RESEARCH APPLIANCE COMPANY

Box 307, Allison Park, Pa.



Bothered by Smoke Control Regulations?

This Little STEP Could Save You Money

The step you see is a positive measurement of the length of time of excessive smoke *accurate to within 6 seconds.*

This record, combined On The Same 24-Hour Chart with a continuous measurement of Smoke Density, gives *a complete permanent record of performance*—visual proof, in an unbeatable pair, of your efforts to comply with the Air Pollution Control Ordinances.

Now you can have such a record—and at a very moderate cost—with the new *Bailey Running Time Recorder* combined with the Bailey Smoke Density Recorder.

You owe it to yourself to investigate this unique pair, exclusive with Bailey and designed to aid you in complying with the Smoke Control Requirements of your community. P37-1

BAILEY METER COMPANY

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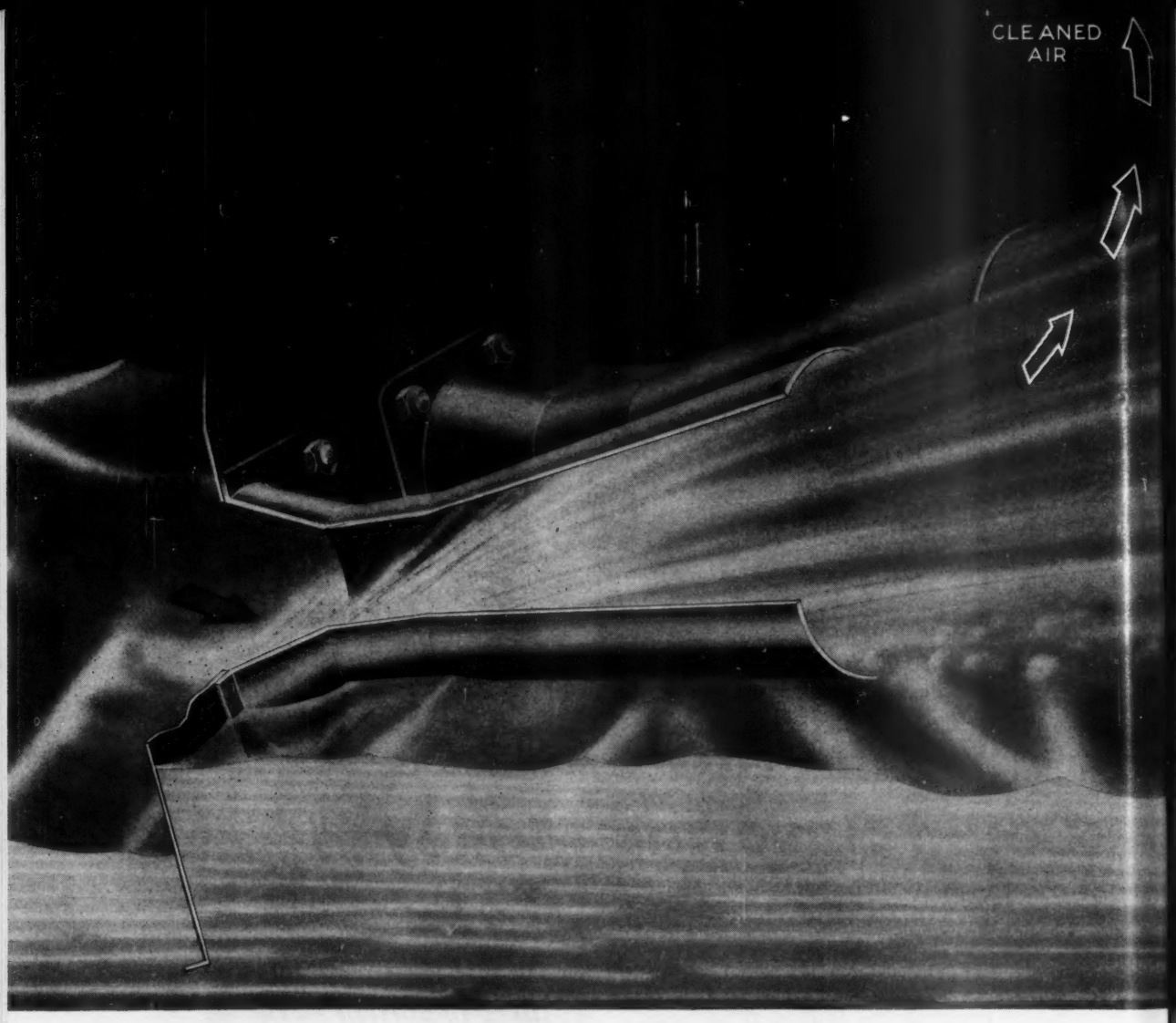
INSTRUMENTS AND CONTROLS

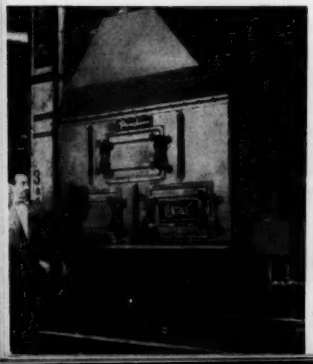
For Power And Process



Puts the squeeze on difficult dusts

Pangborn Ventrijet Wet Dust Collector uses exclusive venturi tubes for peak efficiency

Pangborn Ventrijet Wet Dust Collector on the job. This is just one of Pangborn's comprehensive line of wet and dry dust collectors.



That pinch-necked venturi tube is the secret behind Pangborn Ventrijet performance. As dust-laden air flows through these tubes, the constriction creates a low-pressure area which draws water into the air stream. The resulting turbulence breaks the water into particles which actually *wash* the dust from the air. The simplicity of Ventrijet design saves money in its ease of installation, its low cost of operation and maintenance.

Although the Ventrijet is particularly suited to collecting hot, moist, inflammable, corrosive and obnoxious dusts, the Pangborn engineering it typifies is important to *any* dust-producing plant. It is not enough to put a dust collector within a plant. An efficient dust control system must be *scientifically* planned, designed and constructed to handle effectively a specific dust problem. This thinking is incorporated into every Pangborn proposal.

The Pangborn Engineer in your area will be glad to go to work for you. He is a dust expert *and will discuss your individual problem at no obligation. And, for more information, write for Bulletin 922 to:* Pangborn Corp., *5100 Pangborn Blvd., Hagerstown, Md. Manufacturers of Dust Control and Blast Cleaning Equipment.*

Pangborn CONTROLS DUST

Still ANOTHER Cottrell Advancement By Western Precipitation...

UNIQUE "FULL-RANGE" RAPPER CONTROL PROVIDES ENTIRELY NEW STANDARDS OF VERSATILITY

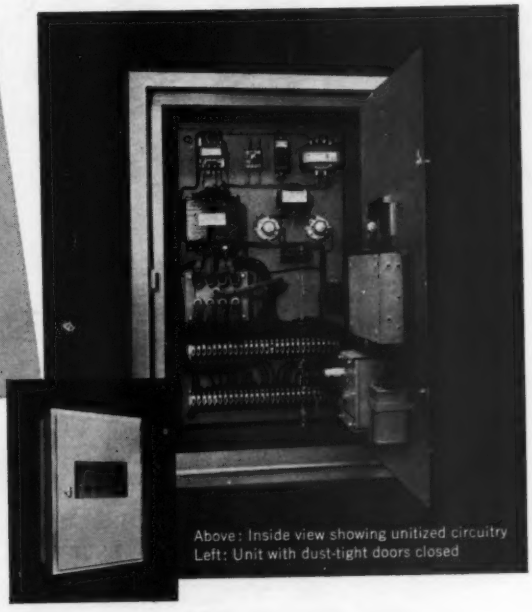
Rapping Frequency...Rapping Intensity...Rapping Pattern
ALL EASILY ADJUSTABLE TO MEET OPERATING REQUIREMENTS

THE PROBLEM:

In the operation of Cottrell Precipitators it is necessary to remove the dust, fume or fly ash that has collected on the plates and cause it to be deposited in a hopper for subsequent removal from the Precipitator. The Rapping System should accomplish this removal with minimum disturbance to the already collected material (to avoid re-entrainment) and with maximum cleaning of the plates.

However, collected materials vary widely in their physical characteristics. Some are sticky. Some agglomerate readily and in thick layers without disrupting electrical operation. Still others have no tendency whatever to agglomerate, but form a sheet of loose particles on the plate.

There is no "typical" dust—no fixed set of conditions to be met. **Yet the Rapper System must be readily adaptable to efficient dust removal, regardless of dust characteristics!**



Above: Inside view showing unitized circuitry
Left: Unit with dust-tight doors closed

THE SOLUTION:

With so many variables to be compensated, unusually wide adjustability of the Rapper System has long been a prime objective for optimum operating efficiency. But complex factors have prevented its attainment until development of Western Precipitation's new "Full Range" Rapper Control.

By simply adjusting a few dials, "Full Range" Control permits:

- **FULL FREQUENCY ADJUSTMENT** from a complete rapping cycle every 50 seconds to one every 3½ hours...or any desired cycle in between!
- **FULL INTENSITY ADJUSTMENT** from zero to maximum over an unusually wide range!
- **FULL PATTERN ADJUSTMENT** 2, 4 or 8 impacts per cycle can be selected, with each cycle varying from light to heavy on successive impacts within the cycle—all automatically controlled to a choice of pre-selected operating limits!

Other Important Advantages...

Greater Safety: The "Full Range" Control has no dangerous high voltage circuits to endanger personnel. Entire unit is in "low-voltage" category.

All "Passive" Design: There are no motors, gears, or other high maintenance components in the "Full Range" Control. It is completely electronic.

Space-Saving Compactness: The "Full Range" Control requires about *half* the space of previous designs. Also is water and dust tight—can be located virtually anywhere.

Unitized Circuitry: All related parts are unitized into separate "cans" for simplified maintenance.

Free! **NEW BROCHURE** which describes and illustrates the new "Full Range" Rapper Control—the latest product of Western Precipitation's program of continuous advancement!

For quick assistance, call or wire **collect** *our nearest office.*

A-N-101

COTTRELL Electrical Precipitators
MULTICLONE Mechanical Collectors
CMP Combination Units
DUALAIRE Jet-Cleaned Filters
THERM-O-FLEX Hi-Temp Filters
TURBULAIRE-DOYLE Scrubbers
HOLO-FLITE Processors
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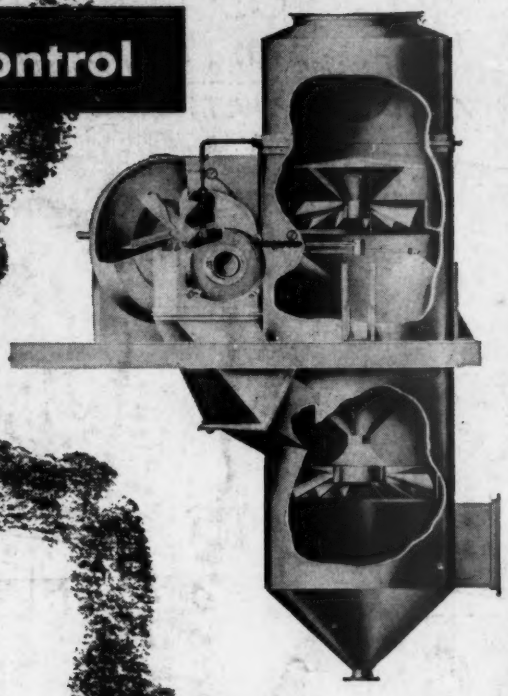
. . . in wet dust control



NEW DUCON DYNAMIC WASHERS

Patented

RECOVER DIFFICULT DUSTS EFFICIENTLY AND ECONOMICALLY

Ducon UW-4 Dynamic Wet Dust Collectors have added a new dimension in dust recovery. They have replaced, with outstanding success, many more costly and less effective dust collectors in the recovery of "difficult" materials, such as fine and abrasive dusts in kilns, rotary driers and other applications.

The UW-4 Washers are also ideal for high loading conditions where maximum efficiency is desired.

Ducon UW-4 washers offer other unique advantages, including constant air capacity, low water consumption and rugged construction. They are self-cleaning and fire and explosion proof.

For complete information write for Bulletin W-7456.

DUST CONTROL SYSTEMS AND EQUIPMENT — DUCON

the name in DUst CONtrol

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Canadian Branch:
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1131 Pettit St., BURLINGTON, ONTARIO

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